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FIELD OF THE INVENTION

The present invention relates to lubricating compositions for fluids used for well drilling or completion operations, or for workover operations in wells. More particularly, the invention describes a process and a composition for
5 controlling the lubricity of water-base fluids set in wellbores.

BACKGROUND OF THE INVENTION

The conventional method for drilling wells, oil wells or not, consists in driving in rotation a toothed bit fastened to the end of a drillpipe string, the string being generally driven in rotation by a surface installation. A fluid,
10 called drilling fluid or mud, is injected at the level of the bit through the inner space of the pipes. The main purposes of this fluid are to clean the bit and the well by taking the debris up to the surface, to stabilize the walls of the well, to inhibit the reactions of the geologic formations in contact with the fluid, etc.

The present invention relates not only to the fluids called drilling fluids,
15 but also to the fluids known as completion fluids, as well as to the fluids called workover fluids, all these fluids being referred to hereafter as well fluids. Completion is an operation which continues the drilling operation when the well reaches the producing formation. Completion notably consists in drilling through the reservoir rock, testing the formation, fitting out the well
20 for production and bringing in. For these operations, the completion fluid may be notably specific to the reservoir rock and to the effluents produced. Workover operations consist in working in a producing well in order to drill, redrill, clean the well or change equipments.

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Well fluids must have characteristics which may be adjusted according to very varied uses, notably their viscosity, their density or their filtrate control capacity. In some cases of strongly deflected wells, horizontal wellbores for example, or more generally wells providing considerable frictions on the tubulars lowered in the well, the lubricity of the fluid becomes an important characteristic.

Documents US-A-4,964,615 and US-A-5,318,956 describe the use of esters of vegetable origin in a mixture for drilling fluids. But none of these documents relates to the optimized composition according to the invention.

10

SUMMARY OF THE INVENTION

The present invention thus relates to a lubricating composition for a well fluid. It includes :

- from 50 % to 99 % by weight of a part A consisting of one or several esters obtained by reaction of a monocarboxylic acid (A.1), linear or branched, including from 8 to 24 carbon atoms, and of a polyol (A.2), linear or branched, including from 2 to 20 carbon atoms,

- from 1 % to 50 % by weight of a part B consisting of one or several monocarboxylic acids, linear or branched, including from 8 to 24 carbon atoms.

20 The polyol A.2 may be, for example, neopentylglycol, pentaerythritol, dipentaerythritol, trimethylolpropane and ditrimethylolpropane.

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The monocarboxylic acid (A.1 and part B) may have 1 to 3 unsaturations and includes 14 to 20 carbon atoms.

The polyol A.2 may have 2 to 5 hydroxyl groups and include from 2 to 6 carbon atoms. Preferably, the polyol may have 4 hydroxyl groups.

- 5 The monocarboxylic acid (A.1 and part B) may be selected from the group made up of oleic, stearic, linoleic, linolenic, palmitic, palmitoleic, myristic acid, and their mixture. The composition may include between 5 and 20 % of part B, preferably about 10 %.

- 10 The acid : alcohol mole ratio (A.1 : A.2) may range between 1 : 1 and $(n-n/10) : 1$, preferably between $(1+n/10) : 1$ and $(n-n/5) : 1$, where n represents the number of hydroxyl groups of the alcohol A.2.

The composition may include between 80 and 95 % of ester A, preferably about 90 %.

- 15 The composition may also include at most 10 % by weight of tertiary amine.

The tertiary amine may be a triethanolamine.

The amount of amine, expressed in molar equivalents with respect to acid B, may range between 0.2 and 1.2.

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The ester part A, the acid part B and the triethanolamine may have respectively the following proportions by weight : about 85.4 %, 9.5 % and 5.1 %.

The composition may include an emulsifying product in a proportion at most equal to 2 % by weight with respect to the composition.

The emulsifying product may be selected from the group made up of RADIASURF 7137 (20 moles ethoxylated sorbitan monolaurate) and RADIASURF 7404 (polyethylene glycol of molecular mass 600).

The invention also relates to a use of the composition according to the invention for controlling the lubricity of a water-base well fluid.

In this use, the added amount of said composition may range between about 0.1 % and 10 % with respect to the fluid.

In case the well fluid is very little charged with reactive solids, the added amount of said composition may range between about 1 % and 3 % with respect to the fluid.

In case the fluid is charged with solids, the added amount of said composition may range between about 3 % and 5 % with respect to the fluid.

The invention also relates to a water-base well fluid including between 0.1 % and 10 %, preferably between 1 % and 5 % by weight of a lubricating composition as that defined in the present invention.

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The applicant has found that the combination of the esters and of the acids in the proportions defined in accordance with the present invention leads to lubricating compositions which are particularly suitable when used in water-base well fluids.

5 According to another embodiment of the present invention, the applicant has found that certain physical properties of the water-base fluids could be even improved by mixing up to 10 % by weight (with respect to the lubricating composition) of one or several tertiary amines into the lubricating composition.

10 According to another embodiment of the present invention, the applicant has found that the addition of up to 2 % by weight (with respect to the lubricating composition) of an emulsifying product often allows the stability properties of the final composition to be improved.

It should be noted that the environmental protection regulations
15 increasingly lay down that the various additives used in the formulation of well fluids have to be nontoxic and nonpolluting with respect to the environment.

The lubricating composition of the present invention notably affords the advantage of meeting the current criteria relating to environmental
20 protection.

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Furthermore, the present composition may be used with all the water-base well fluids, for example bentonite-bearing fluids, weighted up or not, high-pressure/high-temperature (HP/HT) fluids, solid free fluids, etc.

DESCRIPTION OF THE INVENTION

5 Other features and advantages of the invention will be clear from reading the following, non limitative examples.

The lubricity of a lubricating composition according to the invention is tested by means of a "Lubricity tester-Model 212" manufactured by the NL Baroid Petroleum Services company (Instruction Manual Part
10 No.211210001EA). The tests ("Lubricity-surface to surface") are carried out according to the procedures recommended by the standard RP 13B of the American Petroleum Institute (API), (100 psi (689 kPa) at 60 rpm). In order to compare the lubricities of the various compositions, the graduations obtained with the test apparatus described above have been read. These readings
15 correspond to relative values of the friction torque. The lower these read values are, the better the lubricity of the tested composition is.

The principle of the examples hereafter is to add to a base fluid a certain amount of a determined lubricating composition, the mixture being tested thereafter in the apparatus. Unless otherwise specified, the tests have been
20 carried out at ambient temperature (about 25°C).

The lubricating compositions tested hereafter are defined by the following nomenclature :

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L1 corresponds to the ester pentaerythritol monooleate alone, marketed by the FINA company under the trade name of RADIASURF 7156.

L2 corresponds to the mixture by weight of pentaerythritol monooleate and of acid Radiacid 208 in the respective proportions of 85 % and 15 %. The Radiacid 208, marketed by the FINA company, contains about 70 % of oleic acid, 10 % of linoleic acid, 6 % of palmitoleic acid, 5 % of palmitic acid, 4 % of myristic acid, 3 % of linolenic acid and 2 % of stearic acid.

L3 corresponds to a commercial lubricant : "MI-LUBE", marketed by the M.I. company (USA).

L4 corresponds to a commercial lubricant : "LUBRISAL", marketed by the MILLPARK company (USA).

L5 corresponds to gas oil.

L6 corresponds to a mixture of pentaerythritol monooleate and of triethanolamine in the respective proportions of 90 % and 10 %.

L7 corresponds to the mixture by weight of pentaerythritol monooleate, Radiacid 208 and triethanolamine in the respective proportions of 85.4 %, 9.5 % and 5.1 %.

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L8 corresponds to the mixture by weight of pentaerythritol monooleate and of Radiacid 208 in the respective proportions of 90 % and 10 %.

L9 corresponds to the ester 2-ethyl-hexyl oleate.

5 L10 corresponds to the mixture by weight of 2-ethyl-hexyl oleate and of Radiacid 208 in the respective proportions of 85 % and 15 %.

L11 corresponds to the mixture by weight of 2-ethyl-hexyl oleate and of Radiacid 208 in the respective proportions of 90 % and 10 %.

10 L12 corresponds to the mixture by weight of 2-ethyl-hexyl oleate and of Radiacid 208 in the respective proportions of 95 % and 5 %.

L13 corresponds to the system L7 to which 0.15 % by weight of emulsifier RADIASURF 7137 (20 moles ethoxylated sorbitan monolaurate), marketed under this trade name by the FINA company, has been added.

15 L14 corresponds to the system L13 in which the emulsifier is replaced by RADIASURF 7404 (polyethylene monooleate of molecular mass 600), marketed under this trade name by the FINA company.

L2, L7, L8, L13 and L14 correspond to preferred lubricating compositions according to the invention.

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Example No.1 : Case of a conventional freshwater fluid

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- 5 - viscosifier (Xanthan) 2 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate) 3 g/l
- NaOH such that pH = 9

The dispersant is a polyacrylate FP 30S marketed by the COATEX
10 company (France).

The product AQUAPAC Regular is marketed by the AQUALON
company.

The xanthan used for all the tests is the IDVIS marketed by the Dowell
Drilling Fluids company.

15 In this example, the lubricities of various systems are compared : gas oil
(L5), two conventional commercial lubricants (L3, L4) and two systems L1
and L2 based on an ester as defined above.

The various systems have been added to the base fluid which is then
mixed and tested.

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Torque reading

Base fluid		50				
Systems		L1	L2	L3	L4	L5
(%)						
5	0.5		3	39	50	50
	1	4	2	33	7	50
	2	4	1	6	7	50
	3	4	1	5	7	50
	4	4	1	4	7	50
10	5	4	1	4	7	50

The results show the good performances of the system (L2) including two constituents according to the invention. It can be noted that the gas oil (L5) has comparatively a very poor lubricating property.

Example No.2 : Conventional potassium fluid

15 Composition of the base fluid :

	- freshwater	
	- Wyoming bentonite	30 g/l
	- viscosifier (Xanthan)	2 g/l
	- filtrate reducer (AQUAPAC Reg)	1 g/l
20	- dispersant (Polyacrylate FP 30S)	3 g/l
	- KCl	50 g/l
	- NaOH such that	pH = 9

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In this example, the lubricating performances of the systems identical to those of example 1 are compared.

		Torque reading				
Base fluid		44				
5	Systems	L1	L2	L3	L4	L5
	(%)					
	1	44	44	44	44	44
	3	37	10	6	50	44
	4	19	8	6	50	44
10	5	7	3	6	50	44

One observes that, for a KCl fluid, the addition of gas oil or of lubricant L4 does not improve the lubricating properties. The system L1, based on ester alone, is efficient from 4 % onwards. The performances of the system L2 and of the commercial lubricant L3 are the highest from a concentration of about 15 2.5 %.

This example shows the part played by the acid Radiacid 208 in the ester-based composition.

Example No.3 : Conventional fluid in the presence of sodium chloride ,

20 Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- viscosifier (Xanthan) 2 g/l

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- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate FP 30S) 3 g/l
- NaCl 50 g/l
- NaOH such that pH = 9

5 The lubricating performances of systems L1, L2 and L3 are compared in this example.

The measured values are given in the table hereunder :-

		Torque reading		
Base fluid		42		
10	Systems	L1	L2	L3
	(%)			
	0.5	42	5	42
	1	42	2	42
	2	42	2	42
15	3	38	2	14
	4	14	1	4
	5	5	1	4

These results show the very high performances of the system with two constituents L2 in the presence of sodium chloride.

20 Example No.4 : Conventional seawater fluid

Composition of the base fluid :

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- seawater
- Wyoming bentonite 30 g/l
- viscosifier (Xanthan) 2 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate FP-30S) 3 g/l
- NaOH such that pH = 9

The synthetic seawater used is made up of NaCl (28 g/l), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (4.8 g/l), CaCl_2 (1.2 g/l), KCl (1.3 g/l), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (7.2 g/l).

The lubricating performances of systems L1, L2, L3, L4 and L5 are compared in this example.

The measured values are given in the table hereunder :

		Torque reading				
Base fluid		44				
Systems		L1	L2	L3	L4	L5
(%)						
0.5		44	41	44	44	44
1		41	2	42	44	44
2		38	2	42	44	44
3		37	2	38	44	43
4		37	1	37	43	42
5		9	1	36	42	42

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The commercial lubricants L3, L4 and the gas-oil L5 are little efficient with this seawater formulation. It can be seen that the system L1 is efficient from 5 % onwards, whereas the system with two constituents L2 is very efficient as soon as it is added to the formulation at a concentration of 1 %.

Example No.5 : Conventional fluid in the presence of CaCl_2

Composition of the base fluid :

- freshwater	
- Wyoming bentonite	30 g/l
- viscosifier (Xanthan)	2 g/l
- filtrate reducer (AQUAPAC Reg)	1 g/l
- dispersant (Polyacrylate FP 30S)	3 g/l
- CaCl_2	50 g/l
- NaOH such that	pH = 9

In this example, the lubricating performances of the various systems : L3, L1, L2, L7 and L6 are compared.

		Torque reading				
Base fluid		42				
Systems		L1	L2	L3	L6	L7
(%)						
0.5		40	40	42	41	32
1		38	38	42	39	6

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2	36	36	42	38	2
3	36	20	42	36	2
4	6	2	42	34	2
5	5	2	42	14	2

5 These results show that, for this formulation containing CaCl_2 , the ester L1 alone is not very efficient. The mixture L2 shows better performances, but the combination of the three products L7 produces the best results. By comparison, the commercial lubricant L3 is very little efficient. Adding triethanolamine to the ester alone (L6) does not substantially improve the
10 results. The most efficient combinations are ester + acid Radiacid 208 and ester + acid Radiacid 208 + triethanolamine.

Example No.6 : Influence of the triethanolamine concentration in the mixture

15 The influence of the triethanolamine/acid Radiacid 208 molar concentration ratio in the lubricating mixture is tested. The formulation of the base fluid with which the systems are tested corresponds to the formulation of example 5.

20 The base lubricating system is made up of the mixture L8 of pentaerythritol monooleate/acid in the respective proportions of 90 : 10. A certain triethanolamine concentration expressed in molar equivalent with respect to the acid is added to this base system. The systems thus correspond to the following mixtures :

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L8.0 : pentaerythritol monooleate/acid 90 : 10

L8.1 : L8.0 + 0.2 triethanolamine (TEA) molar equivalent

L8.2 : L8.0 + 0.8 TEA equivalent

L8.3 : L8.0 + 1.0 TEA equivalent

5 L8.5 : L8.0 + 1.2 TEA equivalent

L8.6 : L8.0 + 1.4 TEA equivalent.

It may be noted that the mixture L8.3 corresponds to the mixture L7.

		Torque reading					
10	Systems	L8.0	L8.1	L8.2	L8.3	L8.5	L8.6
	(%)						
	1	39	34	26	6	12	39
	2	37	32	4	2	10	14

A synergistic effect of the TEA and of the acid is brought to light by these results.

15 These results show that the performances seem to be optimal when the acid and the triethanolamine molar ratios are close to one another. Furthermore, too high a TEA concentration with respect to the acid decreases the synergistic effect of the acid and of the ester.

20 The triethanolamine (or another tertiary amine) also affords the advantage of decreasing the corrosive effect of the acid (oleic acid for example) in the composition.

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Example No.7 : Influence of the presence of solids in the formulation

The influence, on the lubricating properties, of the addition of barite in the formulation is studied in this example. The purpose of the barite is to increase the density of the mud. The presence of cuttings is also simulated by adding kaolinite and loading clay (FGN) to the formulation.

The lubricating system tested is L7.

The formulation of the base fluid is the formulation of example 4.

As the case may be, one adds barite to this base formulation until a density of 1.4 is obtained, 50 g/l of kaolinite or 50 g/l of loading clays.

10

Torque reading

System L7 (%)	0	0.5	1	2	3	4	5
Base fluid	44	4	2	2	1	1	1
+barite (d=1.4)	44	41	38	2	2	2	1
+kaolinite	44	42	2	2	2	2	1
+FGN		44	41	38	28	1	1
1							
+barite+kaolinite	44	40	30	2	2	2	1
+barite+FGN	44	41	38	33	1	1	1

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FGN is a loading clay marketed by the CKS company.

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The presence of solids in the formulation requires a higher amount of lubricating system, but from 3 % onwards, the results are excellent. In fact, it is well-known that the presence of solids in an aqueous formulation strongly decreases the performances of lubricating systems. It is well-known that very many commercial lubricating systems are little or even not efficient in highly densified fluid formulations.

This test shows that the example L7 of the lubricating composition exhibits excellent lubricating properties in fluids charged with solids insofar as the proportion of said composition is adjusted with respect to the base fluid, particularly in view of the types and amounts of the solids present.

Example No.8 : High pressure/high temperature formulation

Composition of the base fluid :

	- freshwater	
15	- Wyoming bentonite	19 g/l
	- mineral viscosifier (Thermavis)	4.2 g/l
	- filtrate reducer (Thermacheck)	6 g/l
	- dispersant (Thermathin)	19 g/l
	- loading clay (FGN)	50 g/l
20	- barite such that	d = 1.4 (525 g/l)

The products Thermavis, Thermacheck and Thermathin are marketed by the BAROID company (USA). This formulation is proposed for "HP/HT" drilling.

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The lubricating performances of the various systems : L5, L3, L4, L1, L2, L7, L8, L9, L11 and L12 are compared with this formulation.

The results are given hereunder :

5	Systems (%)	Torque reading						
		0	0.5	1	2	3	4	5
	L1	39	39	39	38	37	36	34
	L2	39	37	4	2	2	2	2
	L3	39	38	38	38	10	1	1
10	L4	39	39	40	40	40	39	39
	L5	39	39	39	42	42	42	42
	L7	39	38	32	4	2	2	2
	L8	39	37	35	4	2	2	2
	L9	39	39	40	40	40	40	40
15	L10		39	37	29	12	11	11 10
	L11	39	38	37	23	17	14	13
	L12		39	39	38	36	34	24 19

These tests show that neither the gas oil nor the commercial additive L4 have a lubricating efficiency. The additive L3 only works at a high concentration (from 4 % onwards). The two esters alone (L1 and L9) are not efficient. However, a higher efficiency is observed when they are associated with the acid, the best results being obtained with the pentaerythritol monooleate. An acid Radiacid 208 concentration ranging between 10 and 15 % produces excellent results. However, it may not be advisable to increase the acid concentration too much since it may increase corrosion risks.

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Example No.9 : KCl/PHPA (polyacrylamide) formulation

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- 5 - PHPA (IDCAP) 3 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- KCl 50 g/l
- NaOH such that pH = 9

The product AQUAPAC is marketed by the AQUALON company and
10 the PHPA is a polyacrylamide of trademark IDCAP marketed by the Dowell
Drilling Fluids company.

The lubricating performances of the gas oil (L5), of two conventional
commercial lubricants (L3 and L4) and of system L7 are compared in this
15 example.

Torque reading

	Systems (%)	0	0.5	1	2	3	4
5							
20	L3	38	38	38	25	4	4
	L4	38	38	38	33	31	30
	L5	38	38	38	38	36	35
	L7	38	36	31	10	2	2

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These results show the very good lubricity of system L7.

Example No.10 : Influence of the addition of an emulsifier

Composition of the base fluid :

	- freshwater	
5	- Wyoming bentonite	30 g/l
	- Xanthan (IDVIS)	2 g/l
	- filtrate reducer (AQUAPAC Reg)	1 g/l
	- dispersant (Polyacrylate FP 30S)	3 g/l
	- CaCl_2	50 g/l
10	- NaOH such that	pH = 9

The lubricating performances of the systems L7, L13 and L14 are compared in this example.

The two commercial emulsifiers are surfactants used to stabilize
15 emulsions.

		Torque reading		
Base fluid		42		
Systems		L7	L13	L14
(%)				
20	0.5	32	32	33
	1	6	7	6

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2	2	2	2
3	2	2	2
4	2	2	2
5	2	2	2

5

The following measurements have been performed after weighting the formulation with barite in order to have a density of 1.4.

	Base fluid	Systems (%)	Torque reading		
			42		
10			L7	L13	L14
	0.5	38	38	37	
	1	32	33	32	
	2	29	29	28	
	3	2	2	2	
15	4	2	2	2	
	5	2	2	2	

In both cases, with a nonweighted or a weighted fluid, the addition of an emulsifier does not modify the lubricating capacity of the composition according to the invention.

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Example No.11 : Influence of the addition of an emulsifier in a high pressure/high temperature formulation

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The composition of the base fluid is the same as that in example 8.

		Torque reading		
	Base fluid	39		
	Systems (%)	L7	L13	L14
5	0.5	38	37	37
	1	32	31	31
	2	4	5	4
	3	2	2	2
	4	2	2	2
10	5	2	2	2

The addition of an emulsifier does not modify the lubricity.

Example No.12 : Influence of the addition of a lubricating system on the rheological and filtration properties

15 The composition of the base fluid FB₁ is that of example 10.

One compares in this example the apparent viscosity VA and the plastic viscosity VP in mPa.s, the yield value YV in Pa (to be multiplied by 2.0886 to obtain YV in lb/100ft²), the API filtrate in milliliters (ml), of the base fluid FB, of system L13 and of system L14.

20 Systems L13 and L14 have been mixed with the base fluid in a proportion of 2 % for the following measurements.

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Systems	FB ₁	L13	L14
VA	17	17	16
VP	15	15	14
YV	1.9	1.9	1.9
API filtrate	19.6	13	13.6

The following measurements have been carried out after weighting the formulation with barite to obtain a density of 1.4. The systems L13 and L14 have been mixed with the base fluid in a proportion of 3 %.

Systems	FB ₁	L13	L14
VA	30	26	27
VP	18	16	16
YV	11.5	9.6	10.5
API filtrate	37.4	17.2	18.2

One observes that the lubricating composition does not modify the rheology of the base fluid, weighted or not. On the other hand, the filtrate is markedly improved in both cases.

Example No.13 : Differential pressure sticking test

The tests consist in measuring the friction between the cake obtained by filtration of the fluid and a metallic piston simulating a drill string. The "Differential Sticking Tester-Model 21150" of Baroid Div of NL Corp (Instruction Manual Part No.211510001EA) is used for the tests.

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The operating conditions are as follows: ambient temperature of the fluid, filtration differential pressure 3.5 MPa, pressure on the disk equivalent to 5 MPa, for 10 minutes.

Composition of the base fluid FB_2 :

- 5 - freshwater
- Wyoming bentonite 30 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- NaCl 1 g/l
- Barite such that $d = 1.2$

10 Reference FB_2 corresponds to the base formulation. The various lubricant systems which have been tested are: L5, L3, L4, L1 and L2.

	Formulations	Torque	
		(m.N)	(in.lbs)
	FB_2	31.6	280
15	$FB_2 + 1 \% L5$	21.5	190
	$FB_2 + 2 \% L5$	13.6	120
	$FB_2 + 1 \% L3$	9	80
	$FB_2 + 2 \% L3$	8	70
	$FB_2 + 1 \% L4$	11.3	100
20	$FB_2 + 2 \% L4$	6.8	60
	$FB_2 + 1 \% L1$	5.6	50
	$FB_2 + 2 \% L1$	no sticking	
	$FB_2 + 1 \% L2$	4.5	40
	$FB_2 + 2 \% L2$	no sticking	

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It is obvious that even the composition L1 (ester alone) is more efficient, for the same amount, than the conventional products. The optimized composition L2 exhibits excellent differential pressure antisticking characteristics.

5 Example No.14 : Fluid without reactive clay

Composition of the base fluid :

	- freshwater	
	- Xanthan (IDVIS)	4 g/l
	- filtrate reducer (AQUAPAC Reg)	10 g/l
10	- KCl	50 g/l
	- Barite	30 g/l

		Torque reading				
	Systems (%)	0	0.5	1	2	3
15	L13	32	2	1	1	1
	L3	32	6	5	5	5
	L4	32	12	9	8	8
	L7	32	2	1	1	1

These results show that, even in a fluid formulation without swelling (or
20 reactive) clay, a formulation referred to as "solid free", the lubricating power of the composition according to the present invention, in L13 or L7 form, is excellent in relation to the commercial lubricants.

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A test has been carried out with the same base fluid but without barite,
with the composition L13 :

Systems (%)	Torque reading				
	0	0.5	1	2	3
L13	32	3	2	2	2

Example No.15 : Influence of thermal aging

Composition of the base fluid :

- freshwater	
- Wyoming bentonite	30 g/l
- NaCl	1 g/l

3 % of the lubricating composition L7 or L13 is added to this very simple base formulation. Two fluid samples have been heated to 140°C and 150°C in a hot rolling test cell for 16 hours. After return to ambient temperature (about 25°C), the lubricating power of the fluid samples has been tested in the lubricity tester according to the previous tests :

	25°C	140°C	150°C
L7	1	1	1
L13	1	1	1

This test confirms the excellent temperature strength of the lubricating system according to the invention.

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CLAIMS

1) A lubricating composition for water-base well fluids, characterized in that it includes :

- from 50 % to 99 % by weight of a part A consisting of one or several esters
5 obtained by reaction of a monocarboxylic acid (A.1), linear or branched, including 8 to 24 carbon atoms, and of a polyol (A.2), linear or branched, including 2 to 20 carbon atoms, the acid : alcohol molar ratio (A.1 : A.2) ranges is between 1 : 1 and (n-n/10) : 1, where n represents the number of hydroxyl groups of the alcohol A.2;

- from 1 % to 50 % by weight of a part B consisting of one or several
10 monocarboxylic acids, linear or branched, including 8 to 24 carbon atoms,

and wherein the monocarboxylic acid (A.1 and part B) has 1 to 3 unsaturations.

2) A composition as claimed in claim 1, characterized in that the monocarboxylic
acid (A.1 and part B) includes 14 to 20 carbon atoms.

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3) A composition as claimed in any one of the previous claims, characterized in that said polyol A.2 has 2 to 5 hydroxyl groups and includes 2 to 6 carbon atoms.

4) A composition as claimed in any one of the previous claims, characterized in
20 that said monocarboxylic acid (A.1 and part B) is selected from the group made up of oleic, stearic, linoleic, linolenic, palmitic, palmitoleic, myristic acid and their mixture.

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5) A composition as claimed in any one of the previous claims, characterized in that the acid : alcohol molar ratio (A.1 : A.2) ranges between $(1+n/10) : 1$ and $(n-n/5) : 1$, where n represents the number of hydroxyl groups of the alcohol A.2.

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6) A composition as claimed in any one of the previous claims, characterized in that it includes between 80 % and 95 % of ester A, preferably about 90 %.

7) A composition as claimed in any one of the previous claims, characterized in that it also includes at most 10 % of tertiary amine.

8) A composition as claimed in claim 7, characterized in that said tertiary amine is a triethanolamine.

9) A composition as claimed in any one of claims 7 or 8, characterized in that the amount of said amine, expressed in molar equivalents with respect to the acid B, ranges between 0.2 and 1.2

10) A composition as claimed in any one of claims 7 to 9, characterized in that the ester part A, the acid part B and the triethanolamine have respectively the following proportions by weight : about 85.4 %, 9.5 % and 5.1 %.

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11) A composition as claimed in any one of the previous claims, characterized in that it includes an emulsifying product in a proportion at most equal to 2 % by weight with respect to said composition.

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12) A composition as claimed in claim 11, characterized in that the emulsifying product is selected from the group made up of RADIASURF 7137 (20 moles ethoxylated sorbitan monolaurate) and RADIASURF 7404 (polyethylene glycol monooleate of molecular mass 600).

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13) Use of the composition as claimed in any one of claims 1 to 12 to control the lubricity of a water-base well fluid.

14) Use as claimed in claim 13, characterized in that the added amount of said composition ranges between about 0.1 % and 10 % with respect to the fluid.

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15) Use as claimed in any one of claims 13 or 14, wherein the well fluid is charged with very few reactive solids, characterized in that the added amount of said composition ranges between about 1 % and 3 % with respect to the fluid.

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16) Use as claimed in any one of claims 13 or 14, wherein the fluid is charged with solids, characterized in that the added amount of said composition ranges between about 3 % and 5 % with respect to the fluid.

5 17) Water-base well fluid including between 0.1 % and 10 %, preferably between 1 % and 5 % by weight of a lubricating composition such as that defined in any one of claims 1 to 12.



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PATENT

~~INSTITUT FRANCAIS DU PETROLE~~

FINA RESEARCH S.A.

LUBRICATING COMPOSITION INCLUDING AN ESTER - USE OF
THE COMPOSITION AND WELL FLUID INCLUDING THE
COMPOSITION

Inventors : Jean-François ARGILLIER, Annie AUDIBERT, Pierre
MARCHAND, André DEMOULIN and Michel JANSSEN

ABSTRACT

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- The present invention relates to an optimized lubricating composition including, in useful amount, an ester and a fatty acid.

- In a variant, the composition also includes a tertiary amine, for example a triethanolamine.

- The invention also relates to a well fluid including the lubricating composition according to the invention.

- The invention further relates to a use of the composition for controlling the lubricity of a water-base fluid.

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¹ FIELD OF THE INVENTION

The present invention relates to lubricating compositions for fluids used for well drilling or completion operations, or for workover operations in wells. More particularly, the invention describes a process and a composition for controlling the lubricity of water-base fluids set in wellbores.

BACKGROUND OF THE INVENTION

The conventional method for drilling wells, oil wells or not, consists in driving in rotation a toothed bit fastened to the end of a drillpipe string, the string being generally driven in rotation by a surface installation. A fluid, called drilling fluid or mud, is injected at the level of the bit through the inner space of the pipes. The main purposes of this fluid are to clean the bit and the well by taking the debris up to the surface, to stabilize the walls of the well, to inhibit the reactions of the geologic formations in contact with the fluid, etc.

The present invention relates not only to the fluids called drilling fluids, but also to the fluids known as completion fluids, as well as to the fluids called workover fluids, all these fluids being referred to hereafter as well fluids. Completion is an operation which continues the drilling operation when the well reaches the producing formation. Completion notably consists in drilling through the reservoir rock, testing the formation, fitting out the well for production and bringing in. For these operations, the completion fluid may be notably specific to the reservoir rock and to the effluents produced. Workover operations consist in working in a producing well in order to drill, redrill, clean the well or change equipments.



Well fluids must have characteristics which may be adjusted according to very varied uses, notably their viscosity, their density or their filtrate control capacity. In some cases of strongly deflected wells, horizontal wellbores for example, or more generally wells providing considerable frictions on the tubulars lowered in the well, the lubricity of the fluid becomes an important characteristic.

Documents US-A-4,964,615 and US-A-5,318,956 describe the use of esters of vegetable origin in a mixture for drilling fluids. But none of these documents relates to the optimized composition according to the invention.

SUMMARY OF THE INVENTION

The present invention thus relates to a lubricating composition for a well fluid. It includes :

- from 50 % to 99 % by weight of a part A consisting of one or several esters obtained by reaction of a monocarboxylic acid (A.1), linear or branched, including from 8 to 24 carbon atoms, and of a polyol (A.2), linear or branched, including from 2 to 20 carbon atoms,

- from 1 % to 50 % by weight of a part B consisting of one or several monocarboxylic acids, linear or branched, including from 8 to 24 carbon atoms.

The polyol A.2 may be, for example, neopentylglycol, pentaerythritol, dipentaerythritol, trimethylolpropane and ditrimethylolpropane.

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The monocarboxylic acid (A.1 and part B) may have 1 to 3 unsaturations and includes 14 to 20 carbon atoms.

The polyol A.2 may have 2 to 5 hydroxyl groups and include from 2 to 6 carbon atoms. Preferably, the polyol may have 4 hydroxyl groups.

The monocarboxylic acid (A.1 and part B) may be selected from the group made up of oleic, stearic, linoleic, linolenic, palmitic, palmitoleic, myristic acid, and their mixture. The composition may include between 5 and 20 % of part B, preferably about 10 %.

The acid : alcohol mole ratio (A.1 : A.2) may range between 1 : 1 and $(n-n/10) : 1$, preferably between $(1+n/10) : 1$ and $(n-n/5) : 1$, where n represents the number of hydroxyl groups of the alcohol A.2.

The composition may include between 80 and 95 % of ester A, preferably about 90 %.

The composition may also include at most 10 % by weight of tertiary amine.

The tertiary amine may be a triethanolamine.

The amount of amine, expressed in molar equivalents with respect to acid B, may range between 0.2 and 1.2.

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The ester part A, the acid part B and the triethanolamine may have respectively the following proportions by weight : about 85.4 %, 9.5 % and 5.1 %.

The composition may include an emulsifying product in a proportion at most equal to 2 % by weight with respect to the composition.

The emulsifying product may be selected from the group made up of RADIASURF 7137 (20 moles ethoxylated sorbitan monolaurate) and RADIASURF 7404 (polyethylene glycol of molecular mass 600).

The invention also relates to a use of the composition according to the invention for controlling the lubricity of a water-base well fluid.

In this use, the added amount of said composition may range between about 0.1 % and 10 % with respect to the fluid.

In case the well fluid is very little charged with reactive solids, the added amount of said composition may range between about 1 % and 3 % with respect to the fluid.

In case the fluid is charged with solids, the added amount of said composition may range between about 3 % and 5 % with respect to the fluid.

The invention also relates to a water-base well fluid including between 0.1 % and 10 %, preferably between 1 % and 5 % by weight of a lubricating composition as that defined in the present invention.

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The applicant has found that the combination of the esters and of the acids in the proportions defined in accordance with the present invention leads to lubricating compositions which are particularly suitable when used in water-base well fluids.

According to another embodiment of the present invention, the applicant has found that certain physical properties of the water-base fluids could be even improved by mixing up to 10 % by weight (with respect to the lubricating composition) of one or several tertiary amines into the lubricating composition.

According to another embodiment of the present invention, the applicant has found that the addition of up to 2 % by weight (with respect to the lubricating composition) of an emulsifying product often allows the stability properties of the final composition to be improved.

It should be noted that the environmental protection regulations increasingly lay down that the various additives used in the formulation of well fluids have to be nontoxic and nonpolluting with respect to the environment.

The lubricating composition of the present invention notably affords the advantage of meeting the current criteria relating to environmental protection.

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Furthermore, the present composition may be used with all the water-base well fluids, for example bentonite-bearing fluids, weighted up or not, high-pressure/high-temperature (HP/HT) fluids, solid free fluids, etc.

DESCRIPTION OF THE INVENTION

Other features and advantages of the invention will be clear from reading the following, non limitative examples.

The lubricity of a lubricating composition according to the invention is tested by means of a "Lubricity tester-Model 212" manufactured by the NL Baroid Petroleum Services company (Instruction Manual Part No.211210001EA). The tests ("Lubricity-surface to surface") are carried out according to the procedures recommended by the standard RP 13B of the American Petroleum Institute (API), (100 psi (689 kPa) at 60 rpm). In order to compare the lubricities of the various compositions, the graduations obtained with the test apparatus described above have been read. These readings correspond to relative values of the friction torque. The lower these read values are, the better the lubricity of the tested composition is.

The principle of the examples hereafter is to add to a base fluid a certain amount of a determined lubricating composition, the mixture being tested thereafter in the apparatus. Unless otherwise specified, the tests have been carried out at ambient temperature (about 25°C).

The lubricating compositions tested hereafter are defined by the following nomenclature :

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L1 corresponds to the ester pentaerythritol monooleate alone, marketed by the FINA company under the trade name of RADIASURF 7156.

L2 corresponds to the mixture by weight of pentaerythritol monooleate and of acid Radiacid 208 in the respective proportions of 85 % and 15 %. The Radiacid 208, marketed by the FINA company, contains about 70 % of oleic acid, 10 % of linoleic acid, 6 % of palmitoleic acid, 5 % of palmitic acid, 4 % of myristic acid, 3 % of linolenic acid and 2 % of stearic acid.

L3 corresponds to a commercial lubricant : "MI-LUBE", marketed by the M.I. company (USA).

L4 corresponds to a commercial lubricant : "LUBRISAL", marketed by the MILLPARK company (USA).

L5 corresponds to gas oil.

L6 corresponds to a mixture of pentaerythritol monooleate and of triethanolamine in the respective proportions of 90 % and 10 %.

L7 corresponds to the mixture by weight of pentaerythritol monooleate, Radiacid 208 and triethanolamine in the respective proportions of 85.4 %, 9.5 % and 5.1 %.

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L8 corresponds to the mixture by weight of pentaerythritol monooleate and of Radiacid 208 in the respective proportions of 90 % and 10 %.

L9 corresponds to the ester 2-ethyl-hexyl oleate.

L10 corresponds to the mixture by weight of 2-ethyl-hexyl oleate and of Radiacid 208 in the respective proportions of 85 % and 15 %.

L11 corresponds to the mixture by weight of 2-ethyl-hexyl oleate and of Radiacid 208 in the respective proportions of 90 % and 10 %.

L12 corresponds to the mixture by weight of 2-ethyl-hexyl oleate and of Radiacid 208 in the respective proportions of 95 % and 5 %.

L13 corresponds to the system L7 to which 0.15 % by weight of emulsifier RADIASURF 7137 (20 moles ethoxylated sorbitan monolaurate), marketed under this trade name by the FINA company, has been added.

L14 corresponds to the system L13 in which the emulsifier is replaced by RADIASURF 7404 (polyethylene monooleate of molecular mass 600), marketed under this trade name by the FINA company.

L2, L7, L8, L13 and L14 correspond to preferred lubricating compositions according to the invention.

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Example No.1 : Case of a conventional freshwater fluid

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- viscosifier (Xanthan) 2 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate) 3 g/l
- NaOH such that pH = 9

The dispersant is a polyacrylate FP 30S marketed by the COATEX company (France).

The product AQUAPAC Regular is marketed by the AQUALON company.

The xanthan used for all the tests is the IDVIS marketed by the Dowell Drilling Fluids company.

In this example, the lubricities of various systems are compared : gas oil (L5), two conventional commercial lubricants (L3, L4) and two systems L1 and L2 based on an ester as defined above.

The various systems have been added to the base fluid which is then mixed and tested.

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Torque reading

Base fluid	50				
Systems	L1	L2	L3	L4	L5
(%)					
0.5		3	39	50	50
1	4	2	33	7	50
2	4	1	6	7	50
3	4	1	5	7	50
4	4	1	4	7	50
5	4	1	4	7	50

The results show the good performances of the system (L2) including two constituents according to the invention. It can be noted that the gas oil (L5) has comparatively a very poor lubricating property.

Example No.2 : Conventional potassium fluid

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- viscosifier (Xanthan) 2 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate FP 30S) 3 g/l
- KCl 50 g/l
- NaOH such that pH = 9

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In this example, the lubricating performances of the systems identical to those of example 1 are compared.

Torque reading					
Base fluid	44				
Systems	L1	L2	L3	L4	L5
(%)					
1	44	44	44	44	44
3	37	10	6	50	44
4	19	8	6	50	44
5	7	3	6	50	44

One observes that, for a KCl fluid, the addition of gas oil or of lubricant L4 does not improve the lubricating properties. The system L1, based on ester alone, is efficient from 4 % onwards. The performances of the system L2 and of the commercial lubricant L3 are the highest from a concentration of about 2.5 %.

This example shows the part played by the acid Radiacid 208 in the ester-based composition.

Example No.3 : Conventional fluid in the presence of sodium chloride

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- viscosifier (Xanthan) 2 g/l



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- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate FP 30S) 3 g/l
- NaCl 50 g/l
- NaOH such that pH = 9

The lubricating performances of systems L1, L2 and L3 are compared in this example.

The measured values are given in the table hereunder :-

Base fluid Systems (%)	Torque reading		
	L1	L2	L3
0.5	42	5	42
1	42	2	42
2	42	2	42
3	38	2	14
4	14	1	4
5	5	1	4

These results show the very high performances of the system with two constituents L2 in the presence of sodium chloride.

Example No.4 : Conventional seawater fluid

Composition of the base fluid :

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- seawater
- Wyoming bentonite 30 g/l
- viscosifier (Xanthan) 2 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate FP-30S) 3 g/l
- NaOH such that pH = 9

The synthetic seawater used is made up of NaCl (28 g/l), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (4.8 g/l), CaCl_2 (1.2 g/l), KCl (1.3 g/l), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (7.2 g/l).

The lubricating performances of systems L1, L2, L3, L4 and L5 are compared in this example.

The measured values are given in the table hereunder :

Base fluid	Torque reading				
	44				
Systems	L1	L2	L3	L4	L5
(%)					
0.5	44	41	44	44	44
1	41	2	42	44	44
2	38	2	42	44	44
3	37	2	38	44	43
4	37	1	37	43	42
5	9	1	36	42	42

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The commercial lubricants L3, L4 and the gas-oil L5 are little efficient with this seawater formulation. It can be seen that the system L1 is efficient from 5 % onwards, whereas the system with two constituents L2 is very efficient as soon as it is added to the formulation at a concentration of 1 %.

Example No.5 : Conventional fluid in the presence of CaCl_2

Composition of the base fluid :

- freshwater	
- Wyoming bentonite	30 g/l
- viscosifier (Xanthan)	2 g/l
- filtrate reducer (AQUAPAC Reg)	1 g/l
- dispersant (Polyacrylate FP 30S)	3 g/l
- CaCl_2	50 g/l
- NaOH such that	pH = 9

In this example, the lubricating performances of the various systems : L3, L1, L2, L7 and L6 are compared.

	Torque reading				
Base fluid			42		
Systems	L1	L2	L3	L6	L7
(%)					
0.5	40	40	42	41	32
1	38	38	42	39	6



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2	36	36	42	38	2
3	36	20	42	36	2
4	6	2	42	34	2
5	5	2	42	14	2

These results show that, for this formulation containing CaCl_2 , the ester L1 alone is not very efficient. The mixture L2 shows better performances, but the combination of the three products L7 produces the best results. By comparison, the commercial lubricant L3 is very little efficient. Adding triethanolamine to the ester alone (L6) does not substantially improve the results. The most efficient combinations are ester + acid Radiacid 208 and ester + acid Radiacid 208 + triethanolamine.

Example No.6 : Influence of the triethanolamine concentration in the mixture

The influence of the triethanolamine/acid Radiacid 208 molar concentration ratio in the lubricating mixture is tested. The formulation of the base fluid with which the systems are tested corresponds to the formulation of example 5.

The base lubricating system is made up of the mixture L8 of pentaerythritol monooleate/acid in the respective proportions of 90 : 10. A certain triethanolamine concentration expressed in molar equivalent with respect to the acid is added to this base system. The systems thus correspond to the following mixtures :

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L8.0 : pentaerythritol monooleate/acid 90 : 10

L8.1 : L8.0 + 0.2 triethanolamine (TEA) molar equivalent

L8.2 : L8.0 + 0.8 TEA equivalent

L8.3 : L8.0 + 1.0 TEA equivalent

L8.5 : L8.0 + 1.2 TEA equivalent

L8.6 : L8.0 + 1.4 TEA equivalent.

It may be noted that the mixture L8.3 corresponds to the mixture L7.

Torque reading

Systems	L8.0	L8.1	L8.2	L8.3	L8.5	L8.6
(%)						
1	39	34	26	6	12	39
2	37	32	4	2	10	14

A synergistic effect of the TEA and of the acid is brought to light by these results.

These results show that the performances seem to be optimal when the acid and the triethanolamine molar ratios are close to one another. Furthermore, too high a TEA concentration with respect to the acid decreases the synergistic effect of the acid and of the ester.

The triethanolamine (or another tertiary amine) also affords the advantage of decreasing the corrosive effect of the acid (oleic acid for example) in the composition.



Example No.7 : Influence of the presence of solids in the formulation

The influence, on the lubricating properties, of the addition of barite in the formulation is studied in this example. The purpose of the barite is to increase the density of the mud. The presence of cuttings is also simulated by adding kaolinite and loading clay (FGN) to the formulation.

The lubricating system tested is L7.

The formulation of the base fluid is the formulation of example 4.

As the case may be, one adds barite to this base formulation until a density of 1.4 is obtained, 50 g/l of kaolinite or 50 g/l of loading clays.

System L7 (%)	Torque reading						
	0	0.5	1	2	3	4	5
Base fluid	44	4	2	2	1	1	1
+barite (d=1.4)	44	41	38	2	2	2	1
+kaolinite	44	42	2	2	2	2	1
+FGN		44	41	38	28	1	1
1							
+barite+kaolinite	44	40	30	2	2	2	1
+barite+FGN	44	41	38	33	1	1	1

FGN is a loading clay marketed by the CKS company.



The presence of solids in the formulation requires a higher amount of lubricating system, but from 3 % onwards, the results are excellent. In fact, it is well-known that the presence of solids in an aqueous formulation strongly decreases the performances of lubricating systems. It is well-known that very many commercial lubricating systems are little or even not efficient in highly densified fluid formulations.

This test shows that the example L7 of the lubricating composition exhibits excellent lubricating properties in fluids charged with solids insofar as the proportion of said composition is adjusted with respect to the base fluid, particularly in view of the types and amounts of the solids present.

Example No.8 : High pressure/high temperature formulation

Composition of the base fluid :

- freshwater	
- Wyoming bentonite	19 g/l
- mineral viscosifier (Thermavis)	4.2 g/l
- filtrate reducer (Thermacheck)	6 g/l
- dispersant (Thermathin)	19 g/l
- loading clay (FGN)	50 g/l
- barite such that	$d = 1.4$ (525 g/l)

The products Thermavis, Thermacheck and Thermathin are marketed by the BAROID company (USA). This formulation is proposed for "HP/HT" drilling.



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The lubricating performances of the various systems L5, L3, L4, L1, L2, L7, L8, L9, L11 and L12 are compared with this formulation.

The results are given hereunder :

Systems (%)	Torque reading						
	0	0.5	1	2	3	4	5
L1	39	39	39	38	37	36	34
L2	39	37	4	2	2	2	2
L3	39	38	38	38	10	1	1
L4	39	39	40	40	40	39	39
L5	39	39	39	42	42	42	42
L7	39	38	32	4	2	2	2
L8	39	37	35	4	2	2	2
L9	39	39	40	40	40	40	40
L10		39	37	29	12	11	11 10
L11	39	38	37	23	17	14	13
L12		39	39	38	36	34	24 19

These tests show that neither the gas oil nor the commercial additive L4 have a lubricating efficiency. The additive L3 only works at a high concentration (from 4 % onwards). The two esters alone (L1 and L9) are not efficient. However, a higher efficiency is observed when they are associated with the acid, the best results being obtained with the pentaerythritol monooleate. An acid Radiacid 208 concentration ranging between 10 and 15 % produces excellent results. However, it may not be advisable to increase the acid concentration too much since it may increase corrosion risks.

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Example No.9 : KCl/PHPA (polyacrylamide) formulation

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- PHPA (IDCAP) 3 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- KCl 50 g/l
- NaOH such that pH = 9

The product AQUAPAC is marketed by the AQUALON company and the PHPA is a polyacrylamide of trademark IDCAP marketed by the Dowell Drilling Fluids company.

The lubricating performances of the gas oil (L5), of two conventional commercial lubricants (L3 and L4) and of system L7 are compared in this example.

		Torque reading						
Systems (%)		0	0.5	1	2	3	4	5
L3	38	38	38	25	4	4	4	
L4	38	38	38	33	31	31	30	
L5	38	38	38	38	36	35	33	
L7	38	36	31	10	2	2	2	

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These results show the very good lubricity of system L7.

Example No.10 : Influence of the addition of an emulsifier

Composition of the base fluid :

- freshwater	
- Wyoming bentonite	30 g/l
- Xanthan (IDVIS)	2 g/l
- filtrate reducer (AQUAPAC Reg)	1 g/l
- dispersant (Polyacrylate FP 30S)	3 g/l
- CaCl_2	50 g/l
- NaOH such that	pH = 9

The lubricating performances of the systems L7, L13 and L14 are compared in this example.

The two commercial emulsifiers are surfactants used to stabilize emulsions.

Base fluid	Torque reading		
	L7	L13	L14
Systems			
(%)			
0.5	32	32	33
1	6	7	6



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2	2	2	2
3	2	2	2
4	2	2	2
5	2	2	2

The following measurements have been performed after weighting the formulation with barite in order to have a density of 1.4.

Base fluid Systems (%)	Torque reading		
	L7	L13	L14
0.5	38	38	37
1	32	33	32
2	29	29	28
3	2	2	2
4	2	2	2
5	2	2	2

In both cases, with a nonweighted or a weighted fluid, the addition of an emulsifier does not modify the lubricating capacity of the composition according to the invention.

Example No.11 : Influence of the addition of an emulsifier in a high pressure/high temperature formulation

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The composition of the base fluid is the same as that in example 8.

Base fluid Systems (%)	Torque reading		
	L7	L13	L14
0.5	38	37	37
1	32	31	31
2	4	5	4
3	2	2	2
4	2	2	2
5	2	2	2

The addition of an emulsifier does not modify the lubricity.

Example No.12 : Influence of the addition of a lubricating system on the rheological and filtration properties

The composition of the base fluid FB₁ is that of example 10.

One compares in this example the apparent viscosity VA and the plastic viscosity VP in mPa.s, the yield value YV in Pa (to be multiplied by 2.0886 to obtain YV in lb/100ft²), the API filtrate in milliliters (ml), of the base fluid FB, of system L13 and of system L14.

Systems L13 and L14 have been mixed with the base fluid in a proportion of 2 % for the following measurements.

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Systems	FB ₁	L13	L14
VA	17	17	16
VP	15	15	14
YV	1.9	1.9	1.9
API filtrate	19.6	13	13.6

The following measurements have been carried out after weighting the formulation with barite to obtain a density of 1.4. The systems L13 and L14 have been mixed with the base fluid in a proportion of 3 %.

Systems	FB ₁	L13	L14
VA	30	26	27
VP	18	16	16
YV	11.5	9.6	10.5
API filtrate	37.4	17.2	18.2

One observes that the lubricating composition does not modify the rheology of the base fluid, weighted or not. On the other hand, the filtrate is markedly improved in both cases.

Example No.13 : Differential pressure sticking test

The tests consist in measuring the friction between the cake obtained by filtration of the fluid and a metallic piston simulating a drill string. The "Differential Sticking Tester-Model 21150" of Baroid Div of NL Corp (Instruction Manual Part No.211510001EA) is used for the tests.

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The operating conditions are as follows: ambient temperature of the fluid, filtration differential pressure 3.5 MPa, pressure on the disk equivalent to 5 MPa, for 10 minutes.

Composition of the base fluid FB_2 :

- freshwater
- Wyoming bentonite 30 g/l
- filtrate reducer (AQUAPAC Reg). 1 g/l
- NaCl 1 g/l
- Barite such that $d = 1.2$

Reference FB_2 corresponds to the base formulation. The various lubricant systems which have been tested are : L5, L3, L4, L1 and L2.

Formulations	Torque	
	(m.N)	(in.lbs)
FB_2	31.6	280
$FB_2 + 1 \% L5$	21.5	190
$FB_2 + 2 \% L5$	13.6	120
$FB_2 + 1 \% L3$	9	80
$FB_2 + 2 \% L3$	8	70
$FB_2 + 1 \% L4$	11.3	100
$FB_2 + 2 \% L4$	6.8	60
$FB_2 + 1 \% L1$	5.6	50
$FB_2 + 2 \% L1$	no sticking	
$FB_2 + 1 \% L2$	4.5	40
$FB_2 + 2 \% L2$	no sticking	



It is obvious that even the composition L1 (ester alone) is more efficient, for the same amount, than the conventional products. The optimized composition L2 exhibits excellent differential pressure antisticking characteristics.

Example No.14 : Fluid without reactive clay

Composition of the base fluid :

- freshwater	
- Xanthan (IDVIS)	4 g/l
- filtrate reducer (AQUAPAC Reg)	10 g/l
- KCl	50 g/l
- Barite	30 g/l

		Torque reading				
Systems (%)		0	0.5	1	2	3
L13		32	2	1	1	1
L3	32	6	5	5	5	
L4	32	12	9	8	8	
L7	32	2	1	1	1	

These results show that, even in a fluid formulation without swelling (or reactive) clay, a formulation referred to as "solid free", the lubricating power of the composition according to the present invention, in L13 or L7 form, is excellent in relation to the commercial lubricants.



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A test has been carried out with the same base fluid but without barite,
with the composition L13 :

Systems (%)	Torque reading				
	0	0.5	1	2	3
L13	32	3	2	2	2

Example No.15 : Influence of thermal aging

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- NaCl 1 g/l

3 % of the lubricating composition L7 or L13 is added to this very simple base formulation. Two fluid samples have been heated to 140°C and 150°C in a hot rolling test cell for 16 hours. After return to ambient temperature (about 25°C), the lubricating power of the fluid samples has been tested in the lubricity tester according to the previous tests :

	25°C	140°C	150°C
L7	1	1	1
L13	1	1	1

This test confirms the excellent temperature strength of the lubricating system according to the invention.

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CLAIMS



1) A lubricating composition for water-base well fluids, characterized in that it includes :

- from 50 % to 99 % by weight of a part A consisting of one or several esters obtained by reaction of a monocarboxylic acid (A.1), linear or branched, including 8 to 24 carbon atoms, and of a polyol (A.2), linear or branched, including 2 to 20 carbon atoms, the acid : alcohol molar ratio (A.1 : A.2) ranges is between 1 : 1 and $(n-n/10) : 1$, where n represents the number of hydroxyl groups of the alcohol A.2;

- from 1 % to 50 % by weight of a part B consisting of one or several monocarboxylic acids, linear or branched, including 8 to 24 carbon atoms,

and wherein the monocarboxylic acid (A.1 and part B) has 1 to 3 unsaturations.

2) A composition as claimed in claim 1, characterized in that the monocarboxylic acid (A.1 and part B) includes 14 to 20 carbon atoms.

3) A composition as claimed in any one of the previous claims, characterized in that said polyol A.2 has 2 to 5 hydroxyl groups and includes 2 to 6 carbon atoms.

4) A composition as claimed in any one of the previous claims, characterized in that said monocarboxylic acid (A.1 and part B) is selected from the group made up of oleic, stearic, linoleic, linolenic, palmitic, palmitoleic, myristic acid and their mixture.

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5) A composition as claimed in any one of the previous claims, characterized in that the acid : alcohol molar ratio (A.1 : A.2) ranges between $(1+n/10) : 1$ and $(n-n/5) : 1$, where n represents the number of hydroxyl groups of the alcohol A.2.

6) A composition as claimed in any one of the previous claims, characterized in that it includes between 80 % and 95 % of ester A, preferably about 90 %.

7) A composition as claimed in any one of the previous claims, characterized in that it also includes at most 10 % of tertiary amine.

8) A composition as claimed in claim 7, characterized in that said tertiary amine is a triethanolamine.

9) A composition as claimed in any one of claims 7 or 8, characterized in that the amount of said amine, expressed in molar equivalents with respect to the acid B, ranges between 0.2 and 1.2

10) A composition as claimed in any one of claims 7 to 9, characterized in that the ester part A, the acid part B and the triethanolamine have respectively the following proportions by weight : about 85.4 %, 9.5 % and 5.1 %.



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11) A composition as claimed in any one of the previous claims, characterized in that it includes an emulsifying product in a proportion at most equal to 2 % by weight with respect to said composition.

12) A composition as claimed in claim 11, characterized in that the emulsifying product is selected from the group made up of RADIASURF 7137 (20 moles ethoxylated sorbitan monolaurate) and RADIASURF 7404 (polyethylene glycol monooleate of molecular mass 600).

13) Use of the composition as claimed in any one of claims 1 to 12 to control the lubricity of a water-base well fluid.

14) Use as claimed in claim 13, characterized in that the added amount of said composition ranges between about 0.1 % and 10 % with respect to the fluid.

15) Use as claimed in any one of claims 13 or 14, wherein the well fluid is charged with very few reactive solids, characterized in that the added amount of said composition ranges between about 1 % and 3 % with respect to the fluid.



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16) Use as claimed in any one of claims 13 or 14, wherein the fluid is charged with solids, characterized in that the added amount of said composition ranges between about 3 % and 5 % with respect to the fluid.

17) Water-base well fluid including between 0.1 % and 10 %, preferably between 1 % and 5 % by weight of a lubricating composition such as that defined in any one of claims 1 to 12.



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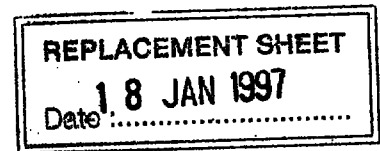
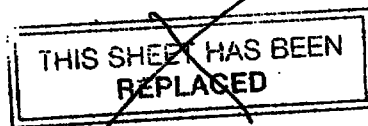
FINA RESEARCH S.A.

**LUBRICATING COMPOSITION INCLUDING AN ESTER - USE OF
THE COMPOSITION AND WELL FLUID INCLUDING THE
COMPOSITION**

Inventors : Jean-François ARGILLIER, Annie AUDIBERT, Pierre
MARCHAND, André DEMOULIN and Michel JANSSEN

ABSTRACT

- The present invention relates to an optimized lubricating composition including, in useful amount, an ester and a fatty acid.
- In a variant, the composition also includes a tertiary amine, for example a triethanolamine.
- The invention also relates to a well fluid including the lubricating composition according to the invention.
- The invention further relates to a use of the composition for controlling the lubricity of a water-base fluid.



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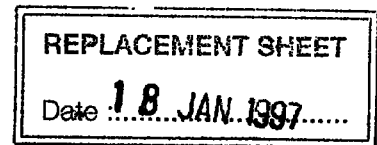
LUBRICATING COMPOSITION INCLUDING AN ESTER-USE OF THE COMPOSITION AND WELL FLUID INCLUDING THE COMPOSITION

The present invention relates to lubricating compositions for fluids used for well drilling or completion operations, or for workover operations in wells. More particularly, the invention describes a process and a composition for controlling the lubricity of water-base fluids set in wellbores.

BACKGROUND OF THE INVENTION

The conventional method for drilling wells, oil wells or not, consists in driving in rotation a toothed bit fastened to the end of a drillpipe string, the string being generally driven in rotation by a surface installation. A fluid, called drilling fluid or mud, is injected at the level of the bit through the inner space of the pipes. The main purposes of this fluid are to clean the bit and the well by taking the debris up to the surface, to stabilize the walls of the well, to inhibit the reactions of the geologic formations in contact with the fluid, etc.

The present invention relates not only to the fluids called drilling fluids, but also to the fluids known as completion fluids, as well as to the fluids called workover fluids, all these fluids being referred to hereafter as well fluids. Completion is an operation which continues the drilling operation when the well reaches the producing formation. Completion notably consists in drilling through the reservoir rock, testing the formation, fitting out the well for production and bringing in. For these operations, the completion fluid may be notably specific to the reservoir rock and to the effluents produced. Workover operations consist in working in a producing well in order to drill, redrill, clean the well or change equipments.



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Well fluids must have characteristics which may be adjusted according to very varied uses, notably their viscosity, their density or their filtrate control capacity. In some cases of strongly deflected wells, horizontal wellbores for example, or more generally wells providing considerable frictions on the tubulars lowered in the well, the lubricity of the fluid becomes an important characteristic.

Documents US-A-4,964,615 and US-A-5,318,956 describe the use of esters of vegetable origin in a mixture for drilling fluids. But none of these documents relates to the optimized composition according to the invention.

SUMMARY OF THE INVENTION

The present invention thus relates to a lubricating composition for a well fluid. It includes :

- from 50 % to 99 % by weight of a part A consisting of one or several esters obtained by reaction of a monocarboxylic acid (A.1), linear or branched, including from 8 to 24 carbon atoms, and of a polyol (A.2), linear or branched, including from 2 to 20 carbon atoms,

- from 1 % to 50 % by weight of a part B consisting of one or several monocarboxylic acids, linear or branched, including from 8 to 24 carbon atoms.

The polyol A.2 may be, for example, neopentylglycol, pentaerythritol, dipentaerythritol, trimethylolpropane and ditrimethylolpropane.

The monocarboxylic acid (A.1 and part B) may have 1 to 3 unsaturations and includes 14 to 20 carbon atoms.

The polyol A.2 may have 2 to 5 hydroxyl groups and include from 2 to 6 carbon atoms. Preferably, the polyol may have 4 hydroxyl groups.

The monocarboxylic acid (A.1 and part B) may be selected from the group made up of oleic, stearic, linoleic, linolenic, palmitic, palmitoleic, myristic acid, and their mixture. The composition may include between 5 and 20 % of part B, preferably about 10 %.

The acid : alcohol mole ratio (A.1 : A.2) may range between 1 : 1 and $(n-n/10) : 1$, preferably between $(1+n/10) : 1$ and $(n-n/5) : 1$, where n represents the number of hydroxyl groups of the alcohol A.2.

The composition may include between 80 and 95 % of ester A, preferably about 90 %.

The composition may also include at most 10 % by weight of tertiary amine.

The tertiary amine may be a triethanolamine.

The amount of amine, expressed in molar equivalents with respect to acid B, may range between 0.2 and 1.2.

The ester part A, the acid part ⁴B and the triethanolamine may have respectively the following proportions by weight : about 85.4 %, 9.5 % and 5.1 %.

The composition may include an emulsifying product in a proportion at most equal to 2 % by weight with respect to the composition.

The emulsifying product may be selected from the group made up of RADIASURF 7137 (20 moles ethoxylated sorbitan monolaurate) and RADIASURF 7404 (polyethylene glycol of molecular mass 600).

The invention also relates to a use of the composition according to the invention for controlling the lubricity of a water-base well fluid.

In this use, the added amount of said composition may range between about 0.1 % and 10 % with respect to the fluid.

In case the well fluid is very little charged with reactive solids, the added amount of said composition may range between about 1 % and 3 % with respect to the fluid.

In case the fluid is charged with solids, the added amount of said composition may range between about 3 % and 5 % with respect to the fluid.

The invention also relates to a water-base well fluid including between 0.1 % and 10 %, preferably between 1 % and 5 % by weight of a lubricating composition as that defined in the present invention.

The applicant has found that the combination of the esters and of the acids in the proportions defined in accordance with the present invention leads to lubricating compositions which are particularly suitable when used in water-base well fluids.

According to another embodiment of the present invention, the applicant has found that certain physical properties of the water-base fluids could be even improved by mixing up to 10 % by weight (with respect to the lubricating composition) of one or several tertiary amines into the lubricating composition.

According to another embodiment of the present invention, the applicant has found that the addition of up to 2 % by weight (with respect to the lubricating composition) of an emulsifying product often allows the stability properties of the final composition to be improved.

It should be noted that the environmental protection regulations increasingly lay down that the various additives used in the formulation of well fluids have to be nontoxic and nonpolluting with respect to the environment.

The lubricating composition of the present invention notably affords the advantage of meeting the current criteria relating to environmental protection.

Furthermore, the present composition may be used with all the water-base well fluids, for example bentonite-bearing fluids, weighted up or not, high-pressure/high-temperature (HP/HT) fluids, solid free fluids, etc.

DESCRIPTION OF THE INVENTION

Other features and advantages of the invention will be clear from reading the following, non limitative examples.

The lubricity of a lubricating composition according to the invention is tested by means of a "Lubricity tester-Model 212" manufactured by the NL Baroid Petroleum Services company (Instruction Manual Part No.211210001EA). The tests ("Lubricity-surface to surface") are carried out according to the procedures recommended by the standard RP 13B of the American Petroleum Institute (API), (100 psi (689 kPa) at 60 rpm). In order to compare the lubricities of the various compositions, the graduations obtained with the test apparatus described above have been read. These readings correspond to relative values of the friction torque. The lower these read values are, the better the lubricity of the tested composition is.

The principle of the examples hereafter is to add to a base fluid a certain amount of a determined lubricating composition, the mixture being tested thereafter in the apparatus. Unless otherwise specified, the tests have been carried out at ambient temperature (about 25°C).

The lubricating compositions tested hereafter are defined by the following nomenclature :

L1 corresponds to the ester ⁷pentaerythritol monooleate alone, marketed by the FINA company under the trade name of RADIASURF 7156.

L2 corresponds to the mixture by weight of pentaerythritol monooleate and of acid Radiacid 208 in the respective proportions of 85 % and 15 %. The Radiacid 208, marketed by the FINA company, contains about 70 % of oleic acid, 10 % of linoleic acid, 6 % of palmitoleic acid, 5 % of palmitic acid, 4 % of myristic acid, 3 % of linolenic acid and 2 % of stearic acid.

L3 corresponds to a commercial lubricant : "MI-LUBE", marketed by the M.I. company (USA).

L4 corresponds to a commercial lubricant : "LUBRISAL", marketed by the MILLPARK company (USA).

L5 corresponds to gas oil.

L6 corresponds to a mixture of pentaerythritol monooleate and of triethanolamine in the respective proportions of 90 % and 10 %.

L7 corresponds to the mixture by weight of pentaerythritol monooleate, Radiacid 208 and triethanolamine in the respective proportions of 85.4 %, 9.5 % and 5.1 %.

L8 corresponds to the mixture⁸ by weight of pentaerythritol monooleate and of Radiacid 208 in the respective proportions of 90 % and 10 %.

L9 corresponds to the ester 2-ethyl-hexyl oleate.

L10 corresponds to the mixture by weight of 2-ethyl-hexyl oleate and of Radiacid 208 in the respective proportions of 85 % and 15 %.

L11 corresponds to the mixture by weight of 2-ethyl-hexyl oleate and of Radiacid 208 in the respective proportions of 90 % and 10 %.

L12 corresponds to the mixture by weight of 2-ethyl-hexyl oleate and of Radiacid 208 in the respective proportions of 95 % and 5 %.

L13 corresponds to the system L7 to which 0.15 % by weight of emulsifier RADIASURF 7137 (20 moles ethoxylated sorbitan monolaurate), marketed under this trade name by the FINA company, has been added.

L14 corresponds to the system L13 in which the emulsifier is replaced by RADIASURF 7404 (polyethylene monooleate of molecular mass 600), marketed under this trade name by the FINA company.

L2, L7, L8, L13 and L14 correspond to preferred lubricating compositions according to the invention.

Example No.1 : Case of a conventional freshwater fluid

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- viscosifier (Xanthan) 2 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate) 3 g/l
- NaOH such that pH = 9

The dispersant is a polyacrylate FP 30S marketed by the COATEX company (France).

The product AQUAPAC Regular is marketed by the AQUALON company.

The xanthan used for all the tests is the IDVIS marketed by the Dowell Drilling Fluids company.

In this example, the lubricities of various systems are compared : gas oil (L5), two conventional commercial lubricants (L3, L4) and two systems L1 and L2 based on an ester as defined above.

The various systems have been added to the base fluid which is then mixed and tested.

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Torque reading

Base fluid	50				
Systems	L1	L2	L3	L4	L5
(%)					
0.5		3	39	50	50
1	4	2	33	7	50
2	4	1	6	7	50
3	4	1	5	7	50
4	4	1	4	7	50
5	4	1	4	7	50

The results show the good performances of the system (L2) including two constituents according to the invention. It can be noted that the gas oil (L5) has comparatively a very poor lubricating property.

Example No.2 : Conventional potassium fluid

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- viscosifier (Xanthan) 2 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate FP 30S) 3 g/l
- KCl 50 g/l
- NaOH such that pH = 9

In this example, the lubricating performances of the systems identical to those of example 1 are compared.

		Torque reading				
Base fluid		44				
Systems		L1	L2	L3	L4	L5
(%)						
1		44	44	44	44	44
3		37	10	6	50	44
4		19	8	6	50	44
5		7	3	6	50	44

One observes that, for a KCl fluid, the addition of gas oil or of lubricant L4 does not improve the lubricating properties. The system L1, based on ester alone, is efficient from 4 % onwards. The performances of the system L2 and of the commercial lubricant L3 are the highest from a concentration of about 2.5 %.

This example shows the part played by the acid Radiacid 208 in the ester-based composition.

Example No.3 : Conventional fluid in the presence of sodium chloride

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- viscosifier (Xanthan) 2 g/l

- filtrate reducer (AQUAPAC Reg)¹² 1 g/l
- dispersant (Polyacrylate FP 30S) 3 g/l
- NaCl 50 g/l
- NaOH such that pH = 9

The lubricating performances of systems L1, L2 and L3 are compared in this example.

The measured values are given in the table hereunder :

Base fluid Systems (%)	Torque reading		
	L1	L2	L3
0.5	42	5	42
1	42	2	42
2	42	2	42
3	38	2	14
4	14	1	4
5	5	1	4

These results show the very high performances of the system with two constituents L2 in the presence of sodium chloride.

Example No.4 : Conventional seawater fluid

Composition of the base fluid :

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- seawater
- Wyoming bentonite 30 g/l
- viscosifier (Xanthan) 2 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate FP 30S) 3 g/l
- NaOH such that pH = 9

The synthetic seawater used is made up of NaCl (28 g/l), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (4.8 g/l), CaCl_2 (1.2 g/l), KCl (1.3 g/l), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (7.2 g/l).

The lubricating performances of systems L1, L2, L3, L4 and L5 are compared in this example.

The measured values are given in the table hereunder :

Base fluid Systems (%)	Torque reading				
	L1	L2	L3	L4	L5
0.5	44	41	44	44	44
1	41	2	42	44	44
2	38	2	42	44	44
3	37	2	38	44	43
4	37	1	37	43	42
5	9	1	36	42	42

The commercial lubricants L3, L¹⁴₄ and the gas oil L5 are little efficient with this seawater formulation. It can be seen that the system L1 is efficient from 5 % onwards, whereas the system with two constituents L2 is very efficient as soon as it is added to the formulation at a concentration of 1 %.

Example No.5 : Conventional fluid in the presence of CaCl_2

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- viscosifier (Xanthan) 2 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate FP 30S) 3 g/l
- CaCl_2 50 g/l
- NaOH such that pH = 9

In this example, the lubricating performances of the various systems : L3, L1, L2, L7 and L6 are compared.

Torque reading					
Base fluid	42				
Systems	L1	L2	L3	L6	L7
(%)					
0.5	40	40	42	41	32
1	38	38	42	39	6

2	36	36	¹⁵ 42	38	2
3	36	20	42	36	2
4	6	2	42	34	2
5	5	2	42	14	2

These results show that, for this formulation containing CaCl_2 , the ester L1 alone is not very efficient. The mixture L2 shows better performances, but the combination of the three products L7 produces the best results. By comparison, the commercial lubricant L3 is very little efficient. Adding triethanolamine to the ester alone (L6) does not substantially improve the results. The most efficient combinations are ester + acid Radiacid 208 and ester + acid Radiacid 208 + triethanolamine.

Example No.6 : Influence of the triethanolamine concentration in the mixture

The influence of the triethanolamine/acid Radiacid 208 molar concentration ratio in the lubricating mixture is tested. The formulation of the base fluid with which the systems are tested corresponds to the formulation of example 5.

The base lubricating system is made up of the mixture L8 of pentaerythritol monooleate/acid in the respective proportions of 90 : 10. A certain triethanolamine concentration expressed in molar equivalent with respect to the acid is added to this base system. The systems thus correspond to the following mixtures :

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L8.0 : pentaerythritol monooleate/acid 90 : 10

L8.1 : L8.0 + 0.2 triethanolamine (TEA) molar equivalent

L8.2 : L8.0 + 0.8 TEA equivalent

L8.3 : L8.0 + 1.0 TEA equivalent

L8.5 : L8.0 + 1.2 TEA equivalent

L8.6 : L8.0 + 1.4 TEA equivalent.

It may be noted that the mixture L8.3 corresponds to the mixture L7.

Systems	Torque reading					
	L8.0	L8.1	L8.2	L8.3	L8.5	L8.6
(%)						
1	39	34	26	6	12	39
2	37	32	4	2	10	14

A synergistic effect of the TEA and of the acid is brought to light by these results.

These results show that the performances seem to be optimal when the acid and the triethanolamine molar ratios are close to one another. Furthermore, too high a TEA concentration with respect to the acid decreases the synergistic effect of the acid and of the ester.

The triethanolamine (or another tertiary amine) also affords the advantage of decreasing the corrosive effect of the acid (oleic acid for example) in the composition.

Example No.7 : Influence of the ¹⁷ presence of solids in the formulation

The influence, on the lubricating properties, of the addition of barite in the formulation is studied in this example. The purpose of the barite is to increase the density of the mud. The presence of cuttings is also simulated by adding kaolinite and loading clay (FGN) to the formulation.

The lubricating system tested is L7.

The formulation of the base fluid is the formulation of example 4.

As the case may be, one adds barite to this base formulation until a density of 1.4 is obtained, 50 g/l of kaolinite or 50 g/l of loading clays.

System L7 (%)	Torque reading						
	0	0.5	1	2	3	4	5
Base fluid	44	4	2	2	1	1	1
+barite (d=1.4)	44	41	38	2	2	2	1
+kaolinite	44	42	2	2	2	2	1
+FGN		44	41	38	28	1	1
1							
+barite+kaolinite	44	40	30	2	2	2	1
+barite+FGN	44	41	38	33	1	1	1

FGN is a loading clay marketed by the CKS company.

The presence of solids in the formulation¹⁸ requires a higher amount of lubricating system, but from 3 % onwards, the results are excellent. In fact, it is well-known that the presence of solids in an aqueous formulation strongly decreases the performances of lubricating systems. It is well-known that very many commercial lubricating systems are little or even not efficient in highly densified fluid formulations.

This test shows that the example L7 of the lubricating composition exhibits excellent lubricating properties in fluids charged with solids insofar as the proportion of said composition is adjusted with respect to the base fluid, particularly in view of the types and amounts of the solids present.

Example No.8 : High pressure/high temperature formulation

Composition of the base fluid :

- freshwater	
- Wyoming bentonite	19 g/l
- mineral viscosifier (Thermavis)	4.2 g/l
- filtrate reducer (Thermacheck)	6 g/l
- dispersant (Thermathin)	19 g/l
- loading clay (FGN)	50 g/l
- barite such that	d = 1.4 (525 g/l)

The products Thermavis, Thermacheck and Thermathin are marketed by the BAROID company (USA). This formulation is proposed for "HP/HT" drilling.

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The lubricating performances of the various systems : L5, L3, L4, L1, L2, L7, L8, L9, L11 and L12 are compared with this formulation.

The results are given hereunder :

Systems (%)	Torque reading						
	0	0.5	1	2	3	4	5
L1	39	39	39	38	37	36	34
L2	39	37	4	2	2	2	2
L3	39	38	38	38	10	1	1
L4	39	39	40	40	40	39	39
L5	39	39	39	42	42	42	42
L7	39	38	32	4	2	2	2
L8	39	37	35	4	2	2	2
L9	39	39	40	40	40	40	40
L10		39	37	29	12	11	11
L11	39	38	37	23	17	14	13
L12		39	39	38	36	34	24

These tests show that neither the gas oil nor the commercial additive L4 have a lubricating efficiency. The additive L3 only works at a high concentration (from 4 % onwards). The two esters alone (L1 and L9) are not efficient. However, a higher efficiency is observed when they are associated with the acid, the best results being obtained with the pentaerythritol monooleate. An acid Radiacid 208 concentration ranging between 10 and 15 % produces excellent results. However, it may not be advisable to increase the acid concentration too much since it may increase corrosion risks.

Example No.9 : KCl/PHPA (polyacrylamide) formulation

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- PHPA (IDCAP) 3 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- KCl 50 g/l
- NaOH such that pH = 9

The product AQUAPAC is marketed by the AQUALON company and the PHPA is a polyacrylamide of trademark IDCAP marketed by the Dowell Drilling Fluids company.

The lubricating performances of the gas oil (L5), of two conventional commercial lubricants (L3 and L4) and of system L7 are compared in this example.

		Torque reading						
Systems (%)		0	0.5	1	2	3	4	5
L3	38	38	38	25	4	4	4	
L4	38	38	38	33	31	31	30	
L5	38	38	38	38	36	35	33	
L7	38	36	31	10	2	2	2	

These results show the very good²¹ lubricity of system L7.

Example No.10 : Influence of the addition of an emulsifier

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- Xanthan (IDVIS) 2 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- dispersant (Polyacrylate FP 30S) 3 g/l
- CaCl_2 50 g/l
- NaOH such that pH = 9

The lubricating performances of the systems L7, L13 and L14 are compared in this example.

The two commercial emulsifiers are surfactants used to stabilize emulsions.

Torque reading

Base fluid		42	
Systems	L7	L13	L14
(%)			
0.5	32	32	33
1	6	7	6

2	2 ²²	2	2
3	2	2	2
4	2	2	2
5	2	2	2

The following measurements have been performed after weighting the formulation with barite in order to have a density of 1.4.

		Torque reading		
Base fluid		42		
Systems (%)		L7	L13	L14
0.5	38	38		37
1	32	33		32
2	29	29		28
3	2	2		2
4	2	2		2
5	2	2		2

In both cases, with a nonweighted or a weighted fluid, the addition of an emulsifier does not modify the lubricating capacity of the composition according to the invention.

Example No.11 : Influence of the addition of an emulsifier in a high pressure/high temperature formulation

The composition of the base fluid²³ is the same as that in example 8.

Base fluid Systems (%)		Torque reading		
		L7	L13	L14
0.5	38	37	37	
1	32	31	31	
2	4	5	4	
3	2	2	2	
4	2	2	2	
5	2	2	2	

The addition of an emulsifier does not modify the lubricity.

Example No.12 : Influence of the addition of a lubricating system on the rheological and filtration properties

The composition of the base fluid FB₁ is that of example 10.

One compares in this example the apparent viscosity VA and the plastic viscosity VP in mPa.s, the yield value YV in Pa (to be multiplied by 2.0886 to obtain YV in lb/100ft²), the API filtrate in milliliters (ml), of the base fluid FB, of system L13 and of system L14.

Systems L13 and L14 have been mixed with the base fluid in a proportion of 2 % for the following measurements.

Systems	FB ₁ ²⁴	L13	L14
VA	17	17	16
VP	15	15	14
YV	1.9	1.9	1.9
API filtrate	19.6	13	13.6

The following measurements have been carried out after weighting the formulation with barite to obtain a density of 1.4. The systems L13 and L14 have been mixed with the base fluid in a proportion of 3 %.

Systems	FB ₁	L13	L14
VA	30	26	27
VP	18	16	16
YV	11.5	9.6	10.5
API filtrate	37.4	17.2	18.2

One observes that the lubricating composition does not modify the rheology of the base fluid, weighted or not. On the other hand, the filtrate is markedly improved in both cases.

Example No.13 : Differential pressure sticking test

The tests consist in measuring the friction between the cake obtained by filtration of the fluid and a metallic piston simulating a drill string. The "Differential Sticking Tester-Model 21150" of Baroid Div of NL Corp (Instruction Manual Part No.211510001EA) is used for the tests.

The operating conditions are as follows : ambient temperature of the fluid, filtration differential pressure 3.5 MPa, pressure on the disk equivalent to 5 MPa, for 10 minutes.

Composition of the base fluid FB_2 :

- freshwater
- Wyoming bentonite 30 g/l
- filtrate reducer (AQUAPAC Reg) 1 g/l
- NaCl 1 g/l
- Barite such that $d = 1.2$

Reference FB_2 corresponds to the base formulation. The various lubricant systems which have been tested are : L5, L3, L4, L1 and L2.

Formulations	Torque	
	(m.N)	(in.lbs)
FB_2	31.6	280
$FB_2 + 1 \% L5$	21.5	190
$FB_2 + 2 \% L5$	13.6	120
$FB_2 + 1 \% L3$	9	80
$FB_2 + 2 \% L3$	8	70
$FB_2 + 1 \% L4$	11.3	100
$FB_2 + 2 \% L4$	6.8	60
$FB_2 + 1 \% L1$	5.6	50
$FB_2 + 2 \% L1$	no sticking	
$FB_2 + 1 \% L2$	4.5	40
$FB_2 + 2 \% L2$	no sticking	

It is obvious that even the composition L1 (ester alone) is more efficient, for the same amount, than the conventional products. The optimized composition L2 exhibits excellent differential pressure antisticking characteristics.

Example No.14 : Fluid without reactive clay

Composition of the base fluid :

- freshwater
- Xanthan (IDVIS) 4 g/l
- filtrate reducer (AQUAPAC Reg) 10 g/l
- KCl 50 g/l
- Barite 30 g/l

		Torque reading				
Systems (%)		0	0.5	1	2	3
L13		32	2	1	1	1
L3	32	6	5	5	5	
L4	32	12	9	8	8	
L7	32	2	1	1	1	

These results show that, even in a fluid formulation without swelling (or reactive) clay, a formulation referred to as "solid free", the lubricating power of the composition according to the present invention, in L13 or L7 form, is excellent in relation to the commercial lubricants.

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A test has been carried out with the same base fluid but without barite, with the composition L13 :

Systems (%)	Torque reading				
	0	0.5	1	2	3
L13	32	3	2	2	2

Example No.15 : Influence of thermal aging

Composition of the base fluid :

- freshwater
- Wyoming bentonite 30 g/l
- NaCl 1 g/l

3 % of the lubricating composition L7 or L13 is added to this very simple base formulation. Two fluid samples have been heated to 140°C and 150°C in a hot rolling test cell for 16 hours. After return to ambient temperature (about 25°C), the lubricating power of the fluid samples has been tested in the lubricity tester according to the previous tests :

	25°C	140°C	150°C
L7	1	1	1
L13	1	1	1

This test confirms the excellent temperature strength of the lubricating system according to the invention.

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CLAIMS



1) A lubricating composition for water-base well fluids, characterized in that it includes :

- from 50 % to 99 % by weight of a part A consisting of one or several esters obtained by reaction of a monocarboxylic acid (A.1), linear or branched, including 8 to 24 carbon atoms, and of a polyol (A.2), linear or branched, including 2 to 20 carbon atoms, the acid : alcohol molar ratio (A.1 : A.2) ranges is between 1 : 1 and $(n-n/10) : 1$, where n represents the number of hydroxyl groups of the alcohol A.2,

- from 1 % to 50 % by weight of a part B consisting of one or several monocarboxylic acids, linear or branched, including 8 to 24 carbon atoms,

and wherein the monocarboxylic acid (A.1 and part B) has 1 to 3 unsaturations.

2) A composition as claimed in claim 1, characterized in that the monocarboxylic acid (A.1 and part B) includes 14 to 20 carbon atoms.

3) A composition as claimed in any one of the previous claims, characterized in that said polyol A.2 has 2 to 5 hydroxyl groups and includes 2 to 6 carbon atoms.

4) A composition as claimed in any one of the previous claims, characterized in that said monocarboxylic acid (A.1 and part B) is selected from the group made up of oleic, stearic, linoleic, linolenic, palmitic, palmitoleic, myristic acid and their mixture.

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5) A composition as claimed in any one of the previous claims, characterized in that the acid : alcohol molar ratio (A.1 : A.2) ranges between $(1+n/10) : 1$ and $(n-n/5) : 1$, where n represents the number of hydroxyl groups of the alcohol A.2.

6) A composition as claimed in any one of the previous claims, characterized in that it includes between 80 % and 95 % of ester A, preferably about 90 %.

7) A composition as claimed in any one of the previous claims, characterized in that it also includes at most 10 % of tertiary amine.

8) A composition as claimed in claim 7, characterized in that said tertiary amine is a triethanolamine.

9) A composition as claimed in any one of claims 7 or 8, characterized in that the amount of said amine, expressed in molar equivalents with respect to the acid B, ranges between 0.2 and 1.2

10) A composition as claimed in any one of claims 7 to 9, characterized in that the ester part A, the acid part B and the triethanolamine have respectively the following proportions by weight : about 85.4 %, 9.5 % and 5.1 %.

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11) A composition as claimed in any one of the previous claims, characterized in that it includes an emulsifying product in a proportion at most equal to 2 % by weight with respect to said composition.

12) A composition as claimed in claim 11, characterized in that the emulsifying product is selected from the group made up of RADIASURF 7137 (20 moles ethoxylated sorbitan monolaurate) and RADIASURF 7404 (polyethylene glycol monooleate of molecular mass 600).

13) Use of the composition as claimed in any one of claims 1 to 12 to control the lubricity of a water-base well fluid.

14) Use as claimed in claim 13, characterized in that the added amount of said composition ranges between about 0.1 % and 10 % with respect to the fluid.

15) Use as claimed in any one of claims 13 or 14, wherein the well fluid is charged with very few reactive solids, characterized in that the added amount of said composition ranges between about 1 % and 3 % with respect to the fluid.

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16) Use as claimed in any one of claims 13 or 14, wherein the fluid is charged with solids, characterized in that the added amount of said composition ranges between about 3 % and 5 % with respect to the fluid.

17) Water-base well fluid including between 0.1 % and 10 %, preferably between 1 % and 5 % by weight of a lubricating composition such as that defined in any one of claims 1 to 12.



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LUBRICATING COMPOSITION INCLUDING AN ESTER - USE OF
THE COMPOSITION AND WELL FLUID INCLUDING THE
COMPOSITION

ABSTRACT

- The present invention relates to an optimized lubricating composition including, in useful amount, an ester and a fatty acid.
- In a variant, the composition also includes a tertiary amine, for example a triethanolamine.
- The invention also relates to a well fluid including the lubricating composition according to the invention.
- The invention further relates to a use of the composition for controlling the lubricity of a water-base fluid.

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CLAIMS

1. A lubricating composition for water-base well fluids, comprising:
from 50% to 99% by weight of a part A consisting of one or several esters obtained by reaction of a monocarboxylic acid (A.1), linear or branched, having 8 to 24 carbon atoms, and of a polyol (A.2), linear or branched, having 2 to 20 carbon atoms, wherein the acid:alcohol molar ratio (A.1:A.2) is between 1:1 and $n-n/10:1$, where n represents the number of hydroxyl groups of the alcohol A.2; and
from 1% to 50% by weight of a part B consisting of monocarboxylic acids, linear or branched, having 8 to 24 carbons atoms;
wherein the monocarboxylic acids in part B are a mixture of at least 80% carboxylic acids having 1 to 3 unsaturations.
2. A composition according to claim 1, wherein the monocarboxylic acid (A.1 and part B) has 14 to 20 carbon atoms.
3. A composition according to claim 1 or claim 2, wherein said polyol A.2 has 2 to 5 hydroxyl groups and has 2 to 6 carbon atoms.
4. A composition according to any one of claims 1 to 3, wherein said monocarboxylic acid (A.1 and part B) comprises oleic or linoleic acid or a mixture thereof.



5. A composition according to any one of the preceding claims, wherein the acid:alcohol molar ratio (A.1:A.2) is between $(1+n/10):1$ and $(n-n/5):1$, where n represents the number of hydroxyl groups of the alcohol A.2.
6. A composition according to any one of the preceding claims, containing between 80% and 95% of ester A.
7. A composition according to any one of the preceding claims, further containing at most 10% of tertiary amine.
8. A composition according to claim 7, wherein said tertiary amine is a triethanolamine.
9. A composition according to claim 7 or claim 8, wherein the amount of said amine, expressed in molar equivalents with respect to the acid B, is 0.2 to 1.2.
10. A composition according to any one of claim 8 or claim 9, wherein the ester part A, the acid part B and the triethanolamine have respectively the following proportions by weight: about 85.4%, 9.5% and 5.1%.
11. A composition according to any one of the preceding claims, further containing an emulsifier in a proportion at most equal to 2% by weight with respect to said composition.



12. A composition according to claim 11, wherein the emulsifier is ethoxylated sorbitan monolaurate or polyethylene glycol monooleate of molecular mass 600.

13. A composition according to claim 6, containing about 90% of ester A.

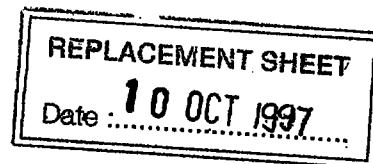
14. A composition according to claim 1, containing at least 3% by weight of part B.

15. A water-base well fluid comprising 0.1% to 10% by weight of a lubricating composition according to any one of claims 1 to 14.

16. A water-base well fluid comprising 1% to 5% by weight of a lubricating composition according to any one of claims 1 to 14.

17. A method for enhancing the lubricity of a water-base well fluid, comprising admixing to said well fluid a composition according to any one of claims 1 to 14.

18. A method according to claim 17, wherein the added amount of said composition is about 0.1% to 10% with respect to the fluid.



19. A method according to claim 17, wherein the well fluid is essentially free of reactive solids, and the added amount of said composition is about 1% to 3% with respect to the fluid.

20. A method according to claim 17, wherein the fluid is charged with solids, and the added amount of said composition is about 3% to 5% with respect to the fluid.

21. A method of enhancing the lubricity of an ester obtained by reaction of a monocarboxylic acid (A.1), linear or branched, having 8 to 24 carbon atoms, and of a polyol (A.2), linear or branched, having 2 to 20 carbon atoms, comprising adding to 50% to 99% by weight of said ester, 1% to 50% by weight of linear or branched monocarboxylic acids (B) having 8 to 24 carbon atoms, wherein the carboxylic acids (B) are a mixture of at least 80% carboxylic acids having 1 to 3 unsaturations.

22. A method according to claim 21, wherein said monocarboxylic acids (B) comprise a mixture of oleic and linoleic acids.