

SPECIFICATION

Oil base emulsion fluids with organophilic clays having enhanced dispersibility

This invention relates to oil-base emulsion fluids containing clay complexes, and more particularly to oil-base emulsion drilling fluids and oil-base emulsion packer fluids containing such clay complexes.

It is well known that organic compounds which contain a cation will react under favorable conditions by ion-exchange with clays which contain a negative layer-lattice and exchangeable cations to form organophilic clay products. If the organic cation contains at least one alkyl group containing at least 10 carbon atoms, the resulting organophilic clays have the property of swelling in certain organic liquids.

Since the commercial introduction of these organophilic clays in the early 1950's under the trademark BENTONE, it has become well known to gain the maximum gelling (thickening) efficiency from these organophilic clays by adding a low molecular weight polar organic material to the composition. Such polar organic materials have been variously called dispersants, dispersion aids, solvating agents, dispersion agents and the like.

The most efficient and accepted polar materials for use as dispersants have been found to be low molecular weight alcohols and ketones, particularly methanol and acetone. These dispersants, however, have very low flash points and require the use of flame-proof apparatus. Higher boiling, high flash point dispersants may be used but these are less efficient and often produce gels having poor secondary properties, such as mechanical stability or storage stability.

The use of organophilic clays as thickeners in petroleum oil for use as oil-base drilling fluids and oil-base packer fluids is well known. Such uses are disclosed in U.S. Patent 2,531,812, U.S. Patent 2,531,427, U.S. Patent 2,966,506, and U.S. Patent 3,831,678. The organophilic clays, however, have been poor gellants for organic systems when incorporated into the system at temperatures less than 55°F (13°C) or when mixed under low shear; some clays have required several hours to achieve significant gelling.

Accordingly, there is a need for an organophilic clay gellant which is easy to disperse in the oil phase of an oil-base emulsion fluid and which achieves substantially complete gellation at low shear in short periods of time.

The present invention provides an oil-base emulsion fluid which comprises an oil phase, a dispersed aqueous phase comprising from 2 to 50% by volume of water and 1 to 30 lbs. per barrel (2.8 to 86 g/l) of an organophilic clay gellant comprising the reaction product of a methyl-benzyl dialkyl ammonium compound, wherein the compound contains 20 to 35% alkyl groups having 16 carbon atoms, and 60 to 75% alkyl groups having 18 carbon atoms and a smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of said clay, and wherein the amount of the ammonium compound is from 80 to 100 milliequivalents per 100 grams of the clay, 100% active clay basis.

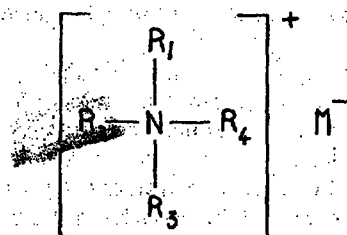
The clays used to prepare the organophilic clay thickeners used in this invention are smectite-type clays which have a cation exchange capacity of at least 75 milliequivalents per 100 grams of clay. Particularly desirable types of the clay are the naturally occurring Wyoming variety of swelling bentonite and like clays, and hectorite, swelling magnesium-lithium-silicate clay.

The clays, especially the bentonite type clays, are preferably converted to the sodium form if they are not already in this form. This can conveniently be done by preparing an aqueous clay slurry and passing the slurry through a bed of cation exchange resin in the sodium form. Alternatively, the clay can be mixed with water and a soluble sodium compound such as sodium carbonate, sodium hydroxide and the like, followed by shearing the mixture in a pugmill or extruder. Mixtures of sodium bentonite and hectorite may be used.

Smectite-type clays prepared synthetically by either a pneumatolytic or, preferably a hydrothermal synthesis process can also be used to prepare the present organophilic clays. Representative of such clays are montmorillonite, bentonite, beidellite, hectorite, saponite and stevensite. These clays may be synthesized hydrothermally by forming an aqueous reaction mixture in the form of a slurry containing mixed hydrous oxides or hydroxides of the desired metals with or without, as the case may be, sodium fluoride or alternate exchangeable cation or mixture thereof in the proportions for the particular synthetic smectite desired. The slurry is then placed in an autoclave and heated under autogenous pressure to a temperature within the range of approximately 100° to 325°C, preferably 274° to 300°C, for a sufficient period of time to form the desired product. Hydrothermal processes for preparing synthetic smectites are described in the following U.S. patents, Granquist 3,252,757; Neumann 3,586,478; Orlemann 3,666,407; Neumann 3,671,190; Hickson 3,844,978; Hickson 3,844,979; Granquist 3,852,405; and Granquist 3,855,147.

The organic compounds used in this invention are quaternary ammonium salts containing one methyl radical, one benzyl radical, and a mixture of alkyl radicals having from 14 to 20 carbon atoms, wherein 20 to 35% have 16 carbon atoms and 60 to 75% have 18 carbon atoms, 100% basis. The salt anion is preferably chloride, bromide, or a mixture thereof, and is more preferably chloride, although other anions such as acetate, hydroxide, nitrate, etc., may be present in the quaternary ammonium salt to neutralize the quaternary ammonium cation. The methyl benzyl dialkyl ammonium salt may be

represented by the formula:



where $R_1 = CH_3$, $R_2 = C_6H_5CH_2$, R_3 and R_4 are alkyl groups containing a mixture of 14 to 20 carbon atoms wherein 20 to 35% have 16 carbon atoms and 60 to 75% have 18 carbon atoms, based on 100%; and where M^- is preferably Cl^- , Br^- , NO_2^- , OH^- , $C_2H_3O_2^-$ or a mixture thereof.

The preferred quaternary amine for use in the practice of this invention is methyl benzyl dihydrogenated tallow ammonium chloride. Commercially prepared hydrogenated tallow typically analyzes 2.0% C_{14} , 0.5% C_{15} , 29.0% C_{16} , 1.5% C_{17} , 66.0% C_{18} , and 1.0% C_{20} alkyl radicals.

The alkyl radicals may be derived from other natural oils including various vegetable oils, such as corn oil, soybean oil, cottonseed oil, castor oil, and the like, and various animal oils or fats. The alkyl radicals may be petrochemically derived such as from alpha olefins.

Many processes are known to prepare methyl benzyl dialkyl ammonium salts. Generally, one skilled in the art would prepare a dialkyl secondary amine, for example, by the hydrogenation of nitriles, see U.S. 2,355,356; form the methyl dialkyl tertiary amine by reductive alkylation using formaldehyde as the source of methyl radical, see Shapiro et. al., U.S. Patent Number 3,136,819; and thereafter form the quaternary amine halide by adding benzyl chloride or benzyl bromide to the tertiary amine, see Shapiro et. al., U.S. Patent Number 2,775,617.

The organophilic clays of this invention can be prepared by mixing the clay, quaternary ammonium compound and water together, preferably at a temperature within the range from 100°F (38°C) to 180°F (82°C), more preferably 140°F (60°C) to 170°F (77°C) for a period of time sufficient for the organic compound to coat the clay particles, followed by filtering, washing, drying and grinding. In using the organophilic clays in emulsions, the drying and grinding steps may be eliminated. When admixing the clay, quaternary ammonium compound and water together in such concentrations that a slurry is not formed, then the filtration and washing steps can be eliminated.

Preferably the clay is dispersed in water at a concentration from about 3% to 7%, the slurry optionally centrifuged to remove non-clay impurities which constitute about 10% to about 50% of the starting clay composition, the slurry agitated and heated to a temperature in the range from 140°F (60°C) to 170°F (77°C) the quaternary amine salt added in the desired milliequivalent ratio, preferably as a liquid in isopropanol or dispersed in water, and the agitation continued to effect the reaction.

The amount of the methyl benzyl dialkyl ammonium salt added to the clay for purposes of this invention must be sufficient to impart to the organophilic clay the enhanced dispersion characteristics desired. The milliequivalent ratio is defined as the number of milliequivalents of the organic compound in the organoclay per 100 grams of clay, 100% active clay basis. The organophilic clays of this invention must have a milliequivalent ratio from 80 to 100 and preferably 85 to 95. At lower milliequivalent ratios, the organophilic clays produced are not effective gellants for oil-base emulsion drilling fluids and oil-base emulsion packer fluids.

In the practice of the present invention, there must be present in the oil-base emulsion fluid an oil phase, a dispersed aqueous phase, and from 1 to 30 lbs. per barrel (2.8 to 86 g/l) of the organophilic clay gellant.

The oil phase useful in preparing the emulsion fluids of this invention may suitably be crude petroleum and fractions thereof, as, for example, diesel oil, kerosene, fuel oil, light lubricating oil fractions, heavy naptha having a boiling range between about 300° to 600°F (149° to 316°C) and the like. The preferred material is diesel oil resulting from a crude distillation of a crude petroleum oil.

The aqueous phase of the invention is water including aqueous solutions of inorganic salts such as sodium chloride, calcium chloride and the like. While the addition of these salts is optional, their presence aids in drilling through formations containing hydratable clays by increasing the osmotic pressure of the water phase. A fuller discussion of the effects of these salts may be found in U.S. Patent 3,561,548.

The exact amount of water incorporated into the fluid is determined by several factors including fluid weight requirements, flow properties desired, bottom-hole temperatures expected to be encountered and the operational requirements placed on the fluid during drilling, coring, or completion operations. In general, we include water in the amount of 2 to 50% by volume. These amounts of water render the oil-base fluid fire-resistant because of the "snuffer" action of the steam bucket released when the oil is exposed to temperatures that would ignite it. In addition, the fluid has excellent tolerance to water contamination; and fluid flow properties can be controlled at values comparable to those of water-base fluids.

Conventional emulsifiers may be employed in the compositions of the invention to emulsify the water in the oil phase. The amount of emulsifier employed is primarily dependent upon the amount of water present and the extent of emulsification desired. Generally from 2 to 30 lbs. per barrel (5.7 to 86 g/l) and preferably from 5 to 20 lbs. per barrel (14 to 57 g/l) have been found satisfactory to achieve the necessary gel strengths and filtration control. The emulsifiers may be selected from conventionally used emulsifiers such as EZ MUL emulsifier and INVERMUL oil mud concentrate, both trademarks of N L Industries, Inc. Baroid Division.

The compositions may optionally contain conventional weighting agents such as BAROID (Registered Trade Mark) barite for controlling fluid density between 7.5 and 22 lb/gal. (21 to 63 g/l) as well as fluid loss control agents (filtrate reducers) such as those described in Jordan et al, U.S. Patent Number 3,168,475 and Andrews et al, U.S. Patent Number 3,494,865.

The amount of the organophilic clay employed is that amount which is effective in obtaining the necessary degree of gellation (thickening) of the oil-base fluid for the intended application, that is, drilling fluid or packer fluid. The minimum concentration of organophilic clay needed to gel any particular composition is dependent upon several factors such as the type of organophilic clay used, the characteristics of the oil phase, and the maximum temperature to which the composition is to be raised. The maximum concentration of organophilic clay which can be used is limited only in that the composition must be sufficiently fluid to be pumpable.

The concentration of organophilic clay within the range of 1 to 30 lbs. per barrel (42 gallon barrel) (2.8 to 86 g/l) will generally provide a sufficiently gelled fluid for broad applications. Preferably 1 to 10 lbs. per barrel (2.8 to 29 g/l) are employed in the preparation of oil-base emulsions drilling fluids whereas amounts from 6 to 30 lbs. per barrel (17 to 86 g/l) have been found adequate for the preparation of oil-base emulsion packer fluids. It has been found that when the organophilic clay is mixed into the oil-base emulsion fluid, substantially complete gelling is achieved at low shear mixing. The resulting oil-base emulsion fluid is a stable oil-base emulsion fluid at surface temperatures below -20°F (-29°C) and down-hole temperatures up to 500°F (260°C). The formation of the stable fluid occurs in a matter of minutes following addition and low shear mixing of the organophilic clay in the oil-base fluid.

A packer fluid is prepared in accordance with this invention by adding to an oil medium the organophilic clay and water optionally containing the inorganic salts in any order. The composition of the packer fluid is regulated as discussed above to provide a pumpable composition. The optional emulsifiers, weighting agents, and fluid loss control materials may be added at any time. It is only necessary to obtain a stable emulsion in the oil phase of the fluid prior to usage of the fluid. Once prepared, the packer fluid is transferred, such as by pumping, into a well bore, at least one portion of which is to be insulated.

The oil-base emulsion drilling fluid can be prepared and used either before drilling commences or while drilling is in progress. The method of adding the ingredient to prepare the fluid is not critical. Mixing is accomplished with conventional devices capable of employing a low shear mixing force. Greater mixing force may be employed even though not necessary. Once prepared, the emulsion drilling fluid is transferred, such as by pumping, into a well bore and circulated to the bit and through the borehole in contact with the walls thereof.

The following examples are given to illustrate the invention, but are not deemed to be limiting thereof. All parts and percentages given are based upon weight unless otherwise indicated. Plastic viscosity, yield point, and ten second gels were measured by the procedure described in API RP 13B, American Petroleum Institutes Standard Procedure For Testing Fluids, 6th Ed., April 1976.

The smectite-type clays used are hectorite and Wyoming bentonite. The hectorite clay was slurried in water and centrifuged to remove substantially all of the non-clay impurities. The Wyoming bentonite clay was slurried in water, centrifuged to remove substantially all of the non-clay impurities, and ion-exchanged to the sodium form by passing the slurry through a bed of cation exchange resin in the sodium form. Several samples of methyl benzyl dihydrogenated tallow ammonium chloride supplied by ENENCO, Inc. were used to prepare the organoclays in the examples. The molecular weight of these samples ranged from 619 to 644, and the percent activity in isopropanol varied from 60% to 81.5%.

Figures quoted herein as "pounds per barrel" are in pounds (Advp.) per petroleum barrel i.e. of 42 U.S. gallons. 1 pound per barrel is equivalent to ca. 2.85 g/l. Gel yield points and gel strengths are quoted in units of pounds per 100 square feet. 1 1/6/100 sq. ft. is equivalent to ca. 4.8 dynes/cm².

The conventionally refined oil and the solvent refined oils had the following properties:

	Conventionally Refined	Solvent Refined
Gravity, °API @ 60°F (15.6°C)	20	30.4
Viscosity, SUS @ 100°F (46.4°C)	500	400
Viscosity, SUS @ 210°F (100°C)	53	58
Viscosity Index	12	98
Index of Refraction	1.5085	1.4811
Flash Point, °F (°C)	390 (199)	460 (238)
Pour Point, °F (°C)	-5 (-20.5)	5 (-15)

EXAMPLE 1

The organophilic clays listed in Table I were prepared by heating the clay slurry to a temperature within the range from 150°F (66°C) to 170°F (77°C), adding while stirring the clay slurry, the indicated amount of the indicated quaternary ammonium chloride which had been previously melted for convenience in handling, and continuing the stirring for approximately 45 minutes, followed by filtering, washing, drying at 140°F (60°C), and grinding.

These organophilic clays were evaluated in the conventionally refined oil in the ease of dispersion test described which dramatically indicates the improved ease of dispersion of these thickeners as compared to similar organophilic clay thickeners.

The data in Table I indicates the sharp increase in the ease of dispersion of organophilic clays prepared from methyl benzyl dihydrogenated tallow ammonium chloride and the smectite-type clays when the amount of this quaternary ammonium compound was in the range of 80 to 100 milliequivalents per 100 grams of clay. The data also illustrates the much superior dispersion characteristics of the inventive organophilic clays as compared with organophilic clays prepared from somewhat similar but different quaternary ammonium compounds.

EXAMPLE 2

The change in physical properties with increasing temperature for a typical oil-base fluid was compared with fluids made according to the invention. The base emulsion fluid was prepared by adding 15 lb-barrel INVERMUL emulsifiers, 2 lb-barrel EZ MUL emulsifier, and DURATONE HT fluid loss control additive, to 220 lb-barrel diesel oil and stirring in a mixer for 2 minutes whereupon 38 lb-barrel water was added and the fluid stirred an additional 8 minutes. BAROID barite and calcium chloride powder were added in amounts of 325 lb-barrel and 19 lb-barrel and the fluid stirred another 10 minutes. The resulting fluid had a density of 14 lb/gal with an 85/15 oil/water volume ratio in the liquid phase.

A portion of the base fluid was divided into two 350 ml aliquots and placed in steel beakers which were packed around with salted ice in a larger container. The samples were stirred at low shear with a MULTI-MIXER until the fluid cooled to 25°F.

A 15 lb-barrel sample of a 95.5 milliequivalent ratio bentonite clay thickener prepared according to Example 1 was stirred in the fluid for 10 minutes. The cold fluid sample was stirred at 600 rpm and gradually heated to 130°F. The same procedure was repeated with a fluid made with 15 lb-barrel of a dimethyldioctadecyl ammonium bentonite clay. The results are set forth in Table II.

The results indicate that the inventive fluids started yielding around 35°F while the conventional fluid did not yield until around 65°F.

EXAMPLE 3

The procedure of Example 2 was repeated with 6 lb-barrel of a bentonite clay thickener having an average milliequivalent ratio of between 82 and 88 and the comparative dimethyldioctadecyl ammonium bentonite clay of Example 2, except that the temperature was maintained at 85°F while the yield point and 10 second gel strengths were measured over a 45 minute time period. The results are set forth in Table III.

The results indicate that the inventive fluid yielded within the first four minutes while the comparative material continued to yield slowly over the entire stirring period and not achieving maximum yield until hot rolled and restirred at high speed.

TABLE I

4.5% Organophilic Clay
10 rpm Brookfield Viscosity, cp.

Organophilic Clay	Quaternary Ammonium Chloride	Clay	ME Ratio	0.12% Water		
				0% Water	6 min.	9 min.
				9.5 min.		
	Methyl benzyl dihydrogenated tallow	Hectorite	87.5	480	----(1)	1,000
	Methyl benzyl dihydrogenated tallow	Hectorite	92.4	480	----	2,000
	Methyl benzyl dihydrogenated tallow	Hectorite	97.2	560	----	9,000
	Methyl benzyl dihydrogenated tallow	Hectorite	99.1	560	----	11,200
	Methyl benzyl dihydrogenated tallow	Hectorite	99.7	---	11,200	---
	Methyl benzyl dihydrogenated tallow	Bentonite	91.5	400	400	---
	Methyl benzyl dihydrogenated tallow	Bentonite	96.9	---	3,200	---
	Dimethyl dihydrogenated tallow	Hectorite	95.2	----	3,400	---
	Dimethyl benzyl hydrogenated tallow	Bentonite	96.6	---	400	---

(1) ---- Indicates the data was not obtained.

TABLE II

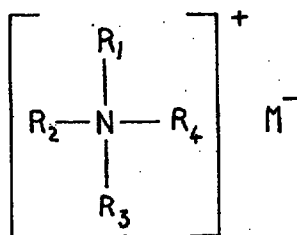
Test Temperature, °F (°C)	Inventive Fluid		Comparative Fluid	
	Yield Point (lb/100 sq ft)	10-Sec Gel (lb/100 sq ft)	Yield Point (lb/100 sq ft)	10-Sec Gel (lb/100 sq ft)
30 (-1)	6	1	6	1
35 (1.3)	8	1	5	0
40 (4.5)	12	2	3	0
45 (7.2)	27	7	4	0
50 (10)	70	32	6	0
55 (12.8)	125	60	8	0
60 (15.6)	130	70	8	2
65 (18.3)	115	70	13	4
70 (21)	125	65	16	6
80 (27)	110	65	17	6
90 (32)	110	55	18	7
100 (38)	55	50	20	9
110 (43)	45	50	22	11
120 (49)	45	50	27	12
130 (54)	45	50	29	14

TABLE III

Test Temperature At 85°F (29.5°C)	Inventive Fluid		Comparative Fluid	
	Yield Point (lb/100 sq ft)	10-Sec Gel (lb/100 sq ft)	Yield Point (lb/100 sq ft)	10-Sec Gel (lb/100 sq ft)
Time: 2 min	30	11	4	1
4 min	37	16	5	2
6 min	38	18	8	2
8 min	37	18	8	3
10 min	39	18	9	4
15 min	39	18	10	4
20 min	39	18	12	5
30 min	38	19	14	6
45 min	38	19	18	8

CLAIMS

1. An oil-base emulsion fluid which comprises an oil phase, a dispersed aqueous phase comprising from 2 to 50% by volume of water and from 1 to 30 lbs. per barrel of an organophilic clay gellant comprising the reaction product of a methyl benzyl dialkyl ammonium compound, wherein the compound contains 20 to 35% alkyl groups having 16 carbon atoms, and 60 to 75% alkyl groups having 18 carbon atoms and a smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of the clay, and wherein the amount of the ammonium compound is from 80 to 100 milliequivalents per 100 grams of the clay, 100% active clay basis.
2. An oil-base emulsion drilling fluid being a fluid as claimed in claim 1 wherein the amount of organophilic clay gellant is from 1 to 10 lbs. per barrel.
3. An oil-base emulsion packer fluid being a fluid as claimed in claim 1 wherein the amount of organophilic clay gellant is from 6 to 30 lbs. per barrel.
4. A fluid as claimed in any one of claims 1 to 3 wherein the smectite-type clay is hectorite, sodium bentonite or a mixture thereof.
5. A fluid as claimed in any one of claims 1 to 4 wherein the amount of ammonium compound is from 85 to 95 milliequivalents per 100 grams of clay.
6. An oil-base emulsion drilling fluid which comprises an oil phase, from 2 to 50% by volume water, and from 1 to 10 lbs. per barrel of an organophilic clay gellant comprising the reaction product of a methyl benzyl dialkyl ammonium compound, wherein the compound contains 20 to 35% alkyl groups having 16 carbon atoms, and 60 to 75% alkyl groups having 18 carbon atoms, and hectorite, sodium bentonite or a mixture thereof, and wherein the amount of the ammonium compound is from 85 to 95 milliequivalents per 100 grams of the clay, 100% active clay basis.
7. An oil-base emulsion packer fluid which comprises an oil phase, from 2 to 50% volume water, and 6 to 30 lbs. per barrel of an organophilic clay gellant comprising the reaction product of a methyl benzyl dialkyl ammonium compound, wherein the compound contains 20 to 35% alkyl groups having 16 carbon atoms, and 60 to 75% alkyl groups having 18 carbon atoms, and hectorite, sodium bentonite or a mixture thereof, and wherein the amount of the ammonium compound is from 85 to 95 milliequivalents per 100 grams of the clay, 100% active clay basis.
8. A fluid as claimed in any one of claims 1 to 7 wherein the ammonium compound is of the formula:



- wherein $R_1 = CH_3$, $R_2 = C_6H_5CH_2$, R_3 and R_4 are alkyl groups containing a mixture of 14 to 20 carbon atoms wherein 20 to 35% have 16 carbon atoms and 60 to 75% have 18 carbon atoms, based on 100% and where M^- is one or more of Cl^- , Br^- , NO_2^- , OH^- , and $C_2H_3O_2^-$.
9. A fluid as claimed in claim 8 wherein the methyl benzyl dialkyl ammonium compound is methyl benzyl dihydrogenated tallow ammonium chloride.
 10. A fluid as claimed in any one of claims 1 to 9 additionally including from 2 to 30 lbs. per barrel of water-in-oil emulsifier.
 11. A fluid as claimed in any one of claims 1 to 10 and substantially as hereinbefore described.
 12. A method of insulating casing in a wellbore which comprises pumping an oil-base emulsion packer fluid in an annular space within the wellbore and thereafter gelling the packer fluid, wherein the packer fluid is a fluid as claimed in any one of claim 3, claims 4, 5 and 8 to 11 when dependent on claim 3, claim 7 and claims 8 to 11 when dependent on claim 7.
 13. A method of drilling a well with a rotary bit which comprises forming a borehole with the bit while circulating through the bit and through the hole in contact with the walls thereof, an oil-base emulsion drilling fluid as claimed in any one of claim 2, claims 4, 5 and 8 to 11 when dependent on claim 2, claim 6 and claims 8 to 11 when dependent on claim 6.
 14. A method of drilling a well or insulating a wellbore casing using a fluid as claimed in any one of claims 1 to 11 and substantially as hereinbefore described.

