

OIL BASE FLUIDS CONTAINING ORGANOPHILIC CLAYS

5 This invention relates to organophilic organic-clay complexes which are dispersible in organic liquids to form a gel therein. More particularly such gels are useful in oil base muds and oil base packer fluids.

10 It is well known that organic compounds containing a cation will react with clays which contain a negative layer-lattice and exchangeable cations to form organophilic organic-clay products. The reaction of an organic cation containing at least one alkyl group of at least 10 carbon atoms with clay generally results in organoclays swellable in certain organic liquids.

15 Prior publications include U.S. Pat. No. 2,531,427, and U.S. Pat. No. 2,966,506 and the book "Clay Mineralogy", 2nd Edition, 1968 by Ralph E. Grim (McGraw Hill Book Co., Inc.), particularly Chapter 10, Clay-Mineral-Organic Reactions; pp. 356-368-Ionic Reactions, Smectite; and pp. 392-401 - Organophilic Clay-Mineral Complexes.

25 Maximum gelling (thickening) efficiency from these organoclays is achieved by adding a low molecular weight polar organic dispersing material to the composition. Such materials are disclosed in U.S. Patents: O'Halloran 2,677,661; McCarthy et al. 2,704,276; Stratton 2,833,720; Stratton 2,879,229; and Stansfield et al. 3,294,683. The use of such dispersion aids was found unnecessary when using particular organophilic clays derived from substituted quaternary ammonium compounds as disclosed in Finlayson et al. 4,105,578 and Finlayson 4,208,218.

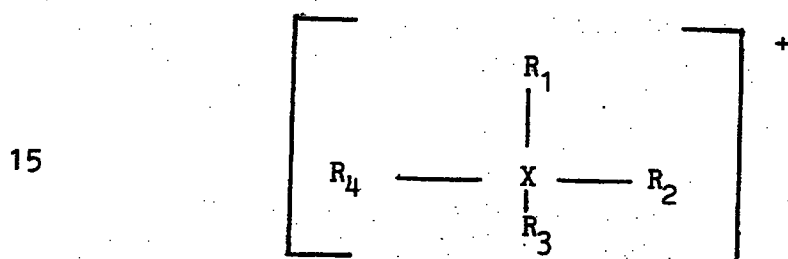
35 Prior organophilic clays have exhibited limited broad range gelling utility due to fluctuating dispersion and viscosity properties. While the materials disclosed in U.S. Patent 4,105,578 have not

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shown such deficiencies, such materials are difficult and costly to produce.

The present invention provides an oil-base fluid comprising an oil phase and from 1 to 50 lbs. per barrel ($2.85-143 \text{ kg}/10^3 \text{ dm}^3$) of an organophilic clay gellant comprising the reaction product of an organic cationic compound and a smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of said clay, wherein the organic cation has the formula:



wherein R_1 is selected from a β, γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms and mixtures thereof; R_2 is a long chain alkyl group having 8 to 60 carbon atoms; R_3 and R_4 are individually selected from a β, γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having from 2 to 6 carbon atoms, an aralkyl group, an alkyl group having from 1 to 22 carbon atoms and mixtures thereof; X is selected from phosphorus and nitrogen; and wherein the amount of the organic cationic compound is from 90 to 140 milliequivalents per 100 grams of said clay, 100% active clay basis.

The oil base fluid of the present invention consists of an oil phase and from 1 to 50 lbs. per barrel ($2.85-143 \text{ kg}/10^3 \text{ dm}^3$) of the organophilic clay gellant. Preferably, the fluid is non-aqueous.

A suitable oil phase of this invention may be crude petroleum and fractions thereof, including but not limited to diesel oil, kerosene, fuel oil, light

lubricating oil fractions, and heavy naphtha having a boiling range from 300° to 600°F. (149°-315°C). The preferred material is diesel oil.

5 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
10 concentration of organophilic clay needed to gel a particular fluid is dependent upon factors such as the type of organophilic clay used, the characteristics of the oil phase and emulsified water phase if any, and the maximum temperature to which the fluid is to be raised. The maximum concentration of organophilic clay
15 is limited to that which will form a pumpable fluid.

The concentration of organophilic clay within the range of 1 to 50 lbs. per barrel (42 gallon barrel) (2.85-143 kg/10³dm³) will generally provide a sufficiently gelled fluid for broad applications.
20 Preferably 1 to 10 lbs. per barrel (2.85-28.6 kg/10³dm³) are employed in the preparation of oil-base drilling fluids whereas amounts from 6 to 50 lbs. per barrel (17.1-143 kg/10³dm³) have been found adequate for the preparation of oil-base packer fluids. It has
25 been found that when the organophilic clay is mixed into the oil-base fluid, essentially complete gelling is achieved at low shear mixing. The resulting oil-base fluid is a stable oil-base fluid at surface temperatures below -20°F (-29°C) and down-hole
30 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.

35 A packer fluid is prepared in accordance with this invention by adding to an oil medium the organophilic clay. 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 fluid prior to usage of the fluid. Once prepared, the packer fluid is transferred, such as by pumping, into an annular space within the well bore.

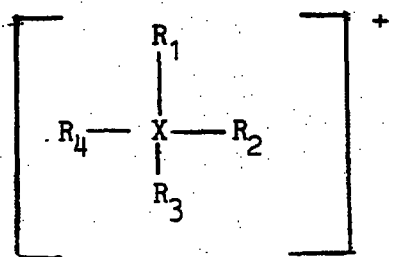
The oil-base drilling fluid can be prepared and used either before drilling commences or while drilling is in progress. The method of adding the ingredient to prepare the fluid is not critical. Mixing is accomplished with conventional devices capable of employing a low shear mixing force. Greater mixing force may be employed even though not necessary. Once prepared, the 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 organophilic clays of this invention can be prepared by admixing the clay, quaternary ammonium compound and water together, preferably at a temperature within the range from 20°C to 100°C, and most preferably from 35°C to 77°C for a period of time sufficient for the organic compound to react with the clay particles, followed by filtering, washing, drying and grinding. The quaternary compound is added in the desired milliequivalent ratio, preferably dispersed in isopropanol or water. In using the organophilic clays in emulsions, the drying and grinding steps may be eliminated. When the clay, quaternary ammonium compound and water are admixed in such concentrations that a slurry is not formed, filtration and washing steps may be eliminated.

The organic cationic compounds useful in this invention may be selected from a wide range of materials that are capable of forming an organophilic clay by exchange of cations with the smectite-type

clay. The organic cationic compound must have a positive charge localized on a single atom or on a small group of atoms within the compound. Preferably the organic cation is selected from the group consisting of quaternary ammonium salts, phosphonium salts, and mixtures thereof, as well as equivalent salts. The organic cation contains at least one member selected from each of two groups, the first group consisting of a β, γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms and mixtures thereof and the second group consisting of a long chain alkyl group.

The organic cation is represented by the formula:



wherein R_1 is selected from the group consisting of a β, γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms and mixtures thereof; R_2 is a long chain alkyl group having 8 to 60 carbon atoms; R_3 and R_4 are selected from a group consisting of a β, γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms, an aralkyl group, an alkyl group having from 1 to 22 carbon atoms and mixtures thereof; and X is phosphorus or nitrogen.

R_1

The β, γ -unsaturated alkyl group may be selected from a wide range of groups. These groups may

be cyclic or acyclic, unsubstituted or substituted. β, γ -unsaturated alkyl groups contain less than 7 aliphatic carbon atoms. The aliphatic group of the β, γ -unsaturated alkyl group preferably contains less than 4 aliphatic carbons. The β, γ -unsaturated alkyl group may be substituted with an aromatic ring that is conjugated with the unsaturation of the β, γ moiety. The β, γ -group may also be substituted with both aliphatic groups and aromatic rings.

Representative examples of cyclic β, γ -unsaturated alkyl groups include 2-cyclohexenyl and 2-cyclopentenyl. Representative examples of acyclic β, γ -unsaturated alkyl groups containing 6 or less carbon atoms include propargyl; 2-propenyl; 2-butenyl; 2-pentenyl; 2-hexenyl; 3-methyl-2-butenyl; 3-methyl-2-pentenyl; 2,3-dimethyl-2-butenyl; 1,1-dimethyl-2-propenyl; 1,2-dimethyl-2-propenyl; 2,4-pentadienyl; and 2,4-hexadienyl. Representative examples of acyclic-aromatic substituted groups include 3-phenyl-2-propenyl; 2-phenyl-2-propenyl; and 3-(4-methoxyphenyl)-2-propenyl. Representative examples of aromatic and aliphatic substituted groups include 3-phenyl-2-cyclohexenyl; 3-phenyl-2-cyclopentenyl. The β, γ -unsaturated alkyl group may be substituted with an aromatic ring.

The hydroxylated group may be a hydroxyl substituted aliphatic radical having from 2 to 6 aliphatic carbons wherein the hydroxyl is not substituted at the carbon adjacent to the positive charged atom. The alkyl group may be substituted with an aromatic ring. Representative examples include 2-hydroxyethyl; 3-hydroxypropyl; 4-hydroxypentyl; 6-hydroxyhexyl; 2-hydroxypropyl; 2-hydroxybutyl; 2-hydroxypentyl; 2-hydroxyhexyl; 2-hydroxycyclohexyl; 3-hydroxycyclohexyl; 4-hydroxycyclohexyl; 2-hydroxycyclopentyl; 3-hydroxycyclopentyl; 2-methyl-2-hydroxypropyl; 3-methyl-2-hydroxybutyl; and 5-hydroxy-2-pentenyl.

R₂

5 The long chain alkyl radicals may be branched or unbranched, saturated or unsaturated, substituted or unsubstituted and have from 8 to 60 carbon atoms in the straight chain portion of the radical.

10 The long chain alkyl radicals may be derived from naturally occurring oils including various vegetable oils, such as corn oil, coconut oil, soybean oil, cottonseed oil, and castor oil and various animal oils and fats such as tallow oil. The alkyl radicals may be derived synthetically from alpha olefins.

15 Representative examples of useful branched, saturated alkyl radicals include 12-methylstearyl; and 12-ethylstearyl. Representative examples of useful branched, unsaturated radicals include 12-methyloleyl and 12-ethyloleyl. Representative examples of unbranched saturated radicals include lauryl; stearyl; tridecyl, myristal (tetradecyl); pentadecyl; hexadecyl; 20 hydrogenated tallow; docosonyl. Representative examples of unbranched, unsaturated and unsubstituted long chain alkyl radicals include oleyl, linoleyl; linolenyl; soya and tallow.

25 R₃ and R₄

R₃ and R₄ are individually selected from a group consisting of (a) a β , γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, described above, (b) a hydroxyalkyl group having 2 to 6 carbon atoms, described above; (c) a cyclic or acyclic alkyl 30 group having 1 to 22 carbon atoms, and (d) an aralkyl group which includes benzyl and substituted benzyl moieties including fused ring moieties having linear or branched chains of 1 to 22 carbon atoms in the alkyl portion of the aralkyl group.

35 The long chain alkyl group of R₃ and R₄ may be linear or branched, cyclic or acyclic, substituted or

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unsubstituted, containing 1 to 22 carbon atoms. Representative examples of useful alkyl groups include methyl; ethyl; propyl; 2-propyl; iso-butyl; cyclopentyl; and cyclohexyl.

5 The alkyl radicals may be derived from sources similar to the long chain alkyl radical of R_2 above.

10 Representative examples of an aralkyl group would include benzyl and those materials derived from compounds such as benzyl halides, benzhydryl halides, trityl halides, 1-halo-1-phenylalkanes wherein the alkyl chain has from 1 to 22 carbon atoms such as 1-halo-1-phenylethane; 1-halo-1-phenyl propane; and 1-halo-1-phenyloctadecane; substituted benzyl moieties
15 such as would be derived from ortho-, meta- and para-chlorobenzyl halides, para-methoxybenzyl halides; ortho-, meta- and para-nitrilobenzyl halides, and ortho-, meta- and para-alkylbenzyl halides wherein the alkyl chain contains from 1 to 22 carbon atoms ; and
20 fused ring benzyl-type moieties such as would be derived from 2-halomethyl-naphthalene, 9-halomethylanthracene and 9-halomethyl-phenanthrene, wherein the halo group would be defined as chloro, bromo, iodo, or any other such group which serves as a
25 leaving group in the nucleophilic attack of the benzyl type moiety such that the nucleophile replaces the leaving group on the benzyl type moiety.

30 A quaternary compound is formed of the above described organic cationic compound and an anionic radical which selected from the group consisting of chloride, bromide, nitrite, hydroxide, acetate and mixtures thereof. Preferably the anion is selected from the group consisting of chloride and bromide, and mixtures thereof, and is more preferably chloride, although other anions such as iodide, acetate,
35 hydroxide and nitrite, may be present in the organic cationic compound to neutralize the cation.

19

Organic cationic salts may be prepared by methods as disclosed in U.S. 2,355,356, 2,775,617 and 3,136,819.

For convenience of handling it is preferred
5 that the total organic content of the organophilic clay reaction products of this invention should be less than 50% by weight of the organoclay. While higher amounts are usable, the reaction product is difficult to filter, dry and grind. The amount of organic cation
10 added to the clay for purposes of this invention must be sufficient to impart to the clay the enhanced dispersion characteristic desired. This amount is defined as the milliequivalent ratio which is the number of milliequivalents (M.E.) of the organic cation in the
15 organoclay per 100 grams of clay, 100% active clay basis. The organophilic clays of this invention must have a milliequivalent ratio from 90 to 140 and preferably 100 to 130. At lower milliequivalent ratios the organophilic clays produced are not effective
20 gellants. At higher milliequivalents ratios the organophilic clays are poor gellants. However, the preferred milliequivalent ratio within the range from 90 to 140 will vary depending on the characteristics of the organic system to be gelled by the organophilic
25 clay.

The manner in which the organic cation functions in the organophilic clay reaction products of this invention is not fully known. The unique properties associated with the compositions of this
30 invention are believed however to relate to the electron withdrawing and donating portions of the cation and particularly to the essential presence of at least one long chain alkyl group coupled with a β , γ -unsaturated alkyl group or a hydroxyalkyl group. When
35 bonded to a positively charged atom the long chain alkyl groups appears to function as an electron donor

which aids in delocalizing the positive charge. More importantly however it enables the clay platelets to be separated sufficiently to allow further separation under moderate shear conditions. In contrast, the β, γ -unsaturated alkyl group appears to create a delocalization of the positive charge which may result from a resonance or inductive effect occurring with the unsaturated alkyl group. This effect does not occur to any significant extent with other prior art saturated alkyl groups. The enhanced function of the short chain hydroxyalkyl group appears to be related to the internal covalent bonded polar activating moiety, namely the hydroxyly group when not adjacent the positive charged atom. This effect is negated when the hydroxyl moiety is located on a carbon atom adjacent to the positive charged atom or on an alkyl group greater than 6 carbon atoms.

Suitable smectite-type clays occur naturally or may be prepared synthetically. Such clays include montmorillonite, bentonite, beidellite, hectorite, saponite, and stevensite. In particular smectite-type clays should have a cation exchange capacity of at least 75 milliequivalents per 100 grams of clay. Particularly desirable types of clay are the naturally-occurring Wyoming varieties of bentonite and hectorite, a magnesium-lithium silicate clay. Suitable clays may also be synthesized by conventional means including pneumatolitic and hydrothermal methods.

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 compound such as sodium carbonate and sodium hydroxide followed by shearing the mixture

with a pugmill or extruder.

The cation exchange capacity of the smectite-type clays can be determined by the ammonium acetate method.

5 The clay is preferably dispersed in water in a weight concentration ranging from 1 to 80% and preferably from 2% to 20%, and more preferably from 2% to 7%. The slurry is agitated prior to reaction.

10 The organic cationic compounds of the invention were prepared by standard prior art methods starting with an amine having the desired number of long chain alkyl groups bonded to the nitrogen atom. This long chain alkyl amine was then reacted by reductive alkylation with an aldehyde or by nucleophilic
15 displacement of an alkyl halide to form the desired quaternary ammonium compound.

20 The fluid of this invention may contain an aqueous phase which includes aqueous solutions of inorganic salts such as sodium chloride and calcium chloride. While addition of these salts is optional, such salts increase the osmotic pressure of the water phase to stabilize formations containing hydratable clays.

25 The concentration of water in the fluid is determined by factors such as fluid weight requirements, flow properties desired, bottom-hole temperatures and the operational requirements of drilling, coring, or completion. In general, it has been found preferably to employ a volume percent of
30 water ranging from 2 to 50%. This range renders the oil-base fluid fire-resistant upon exposure 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
35 comparable to those of water-based fluids.

In using an aqueous phase in the fluid,

conventional emulsifiers should be employed for the water-in-oil phase. In the non-aqueous fluid, emulsifiers may also be used. The amount of emulsifier employed is primarily dependent upon the amount of
5 water present and the extent of emulsification desired. Generally from 1 to 30 lbs. per barrel ($2.85-85.7 \text{ kg}/10^3 \text{ dm}^3$) and preferably from 1 to 15 lbs. per barrel ($2.85-42.8 \text{ kg}/10^3 \text{ dm}^3$) have been found satisfactory to achieve the emulsion stability.

10 The compositions may optionally contain conventional weighting agents such as barite for controlling fluid density between 7.5 and 22 lb/gal ($0.9-2.6 \text{ kg}/\text{dm}^3$) as well as fluid loss control agents.

The smectite-type clays used in the Examples
15 were hectorite and Wyoming bentonite. The clay was slurried in water and centrifuged to remove essentially all of the non-clay impurities which may amount to 10% to 50% of the starting clay composition. The Wyoming bentonite clay slurry was passed through a bed of
20 cation exchange resin to convert it to the sodium form.

The organic cationic compounds exemplified are representative of the cations of the invention and are not intended to be inclusive of the only operative compounds. The following examples are given to
25 illustrate the invention, but are not deemed to be limiting thereof.

All percentages given are based upon weight unless otherwise indicated. Plastic viscosity, yield point, and ten second gels were measured by the
30 procedure described in API RP13B, American Petroleum Institutes Standard Procedure for Testing Fluids, 6th Ed., April 1976. Barrels (bbl) and gallons are U.S. measure.

Example 1

35 Allyl methyl di(hydrogenated-tallow)ammonium chloride (abbreviated AM2HT).

824.7 g methyl di(hydrogenated-tallow) amine, 350 ml isopropyl alcohol, 250 g NaHCO_3 , 191.3 g allyl chloride, and 10 g allyl bromide (as a catalyst) are placed in a 4-liter reaction vessel equipped with a condenser, the mixture is heated and allowed to reflux. A sample was removed, filtered, and titrated with HCl and NaOH. The reaction was considered complete at 0.0% amine HCl and 1.8% amine. The final analysis showed an effective gram molecular weight of 831.17.

Examples 2-4

A 3% clay slurry, the sodium form of Wyoming bentonite for Examples 2 and 3 and hectorite for Example 4, was heated to 60°C with stirring. An isopropyl alcohol solution of organic cationic compound, ethanol methyl di(hydrogenated tallow) ammonium chloride [EM2HT] - (Arnak Co. Division of Akzona Corp.) at 80% activity in Example 2 and AM2HT, prepared in Example 1, for Examples 3 and 4 was added to the clay slurry and stirred for 20 minutes. The organoclay was collected on a vacuum filter. The filter cake was washed with 60° water and dried at 60°C. The dried organoclay was ground using a hammer mill to reduce the particle size and sieved through a U.S. Standard 200 mesh screen.

Examples 5-8

0.63 bbl (100 dm³) of diesel oil, 8 pounds (3.6 kg) emulsifier (Invermul, NL Industries, Inc.), 8 pounds (3.6 kg) filtration control, amine lignite (Duratone HT, NL Industries, Inc.) 4 pounds (1.8 kg) lime, 0.11 bbl (17.5 dm³) of water was stirred for 20 minutes.

22 Pounds (10 kg) of calcium chloride, 325 pounds (148 kg) of barrite (Baroid, NL Industries, Inc.) and 5 pounds (2.3 kg) of the two bentonite clay



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thickeners prepared in Examples 2 and 3 in addition to two commercial products, dimethyl di(hydrogenated-

tallow) ammonium chloride [2M2HT] 7 bentonite and benzyl methyl di(hydrogenated-tallow) ammonium chloride [BM2HT]/bentonite.

5 The mixed fluid was tested at 95°F. (35°C) for standard rheology data and the results are shown in Table 1. None of the Examples settled following stirring:

Table 1

Example No.	Gellant Compound	Yield Point	10 sec. Gel	10 min. Gel
		lbs/100ft ² (kg/m ²)	lbs/100ft ² (kg/m ²)	lbs/100ft ² (kg/m ²)
5	EM2HT/bentonite	18 (8.8)	9 (4.4)	13 (6.4)
6	AM2HT/bentonite	20 (9.8)	11 (5.4)	14 (6.9)
7	2M2HT/bentonite	30 (14.7)	16 (7.8)	19 (9.3)
8	BM2HT/bentonite	24 (11.8)	14 (6.9)	18 (8.8)

15 The unstirred batches of Examples 5-8 were rolled at 150°F (66°C) for 16 hours and no settling was noted in any Example. The batches were tested at 80°F (27°C) for standard rheology data as in Example 5. The results are shown in Table 2 below.

20 None of the Examples settled.

Table 2

Example No.	Yield Point	10 sec. Gel	10 min. Gel
	lbs/100ft ² (kg/m ²)	lbs/100ft ² (kg/m ²)	lbs/100ft ² (kg/m ²)
5	19 (9.3)	9 (4.4)	14 (6.9)
6	17 (8.3)	12 (5.9)	15 (7.4)
7	20 (9.8)	13 (6.4)	18 (8.8)
8	21 (10.3)	14 (6.9)	19 (9.3)

Examples 9-13

350 ml. batches of fluids consisting of 0.60 bbl (95.4 dm³) of diesel oil, 8 pounds (3.6 kg) emulsifier (Invermul, NL Industries, Inc.), 8 pounds (3.6 kg) amine lignite filtration control aid 5 (Duratone, NL Industries, Inc.), 5 pounds (2.3 kg) lime, 0.20 bbl (31.8 dm³) of 11.0 lbs per gallon, (1.32 kg/dm³), aqueous calcium chloride, 320 pounds (45.3 kg) of barite (Baroid, NL Industries, Inc.) was admixed, stirred for 15 minutes in a Hamilton Beach 10 mixer and cooled to 28°F (-2.2°C) in an ice bath. A 6 lb/bbl (17.4 kg/10³dm³) concentration of the clays EM2HT/bentonite, AM2HT/bentonite and AM2HT/hectorite produced in Examples 2, 3, and 4 respectively in addition to two commercial clays 2M2HT/bentonite 15 and BM2HT/bentonite described in Examples 7 and 8 were stirred into the cold fluid batches over a 5 minute period at low shear with a Lightning mixer. The cold examples in a viscometer cup, were placed on a Fann 35 viscometer and stirred at 600 rpm while the temperature 20 rose to 70°F (21°C). The batches were then placed in a preheated cup jackets set at 125°F (51.7°C) and allowed to heat to 110°F (43.3°C). The plastic viscosity, yield point and 10-sec gel were measured at every 5°F increment between 30 to 70°F (-1.1°C-21°C) and at every 25 10°F increment between 70 to 100°F (21°C-43.3°C). The results of the measurements are presented in Figure 1.

Examples 13-17 at 115°F (46°C) were stirred for 15 minutes in a Hamilton Beach mixer and cooled to 80°F (27°C) and tested as with Example 5. The results are 30 presented in Table 3 below.

28

Table 3

Example	No.	Yield Point <u>lbs/</u>	10 sec. Gel <u>lbs/</u>	10 min. Gel <u>lbs/</u>
		<u>100ft²(kg/m²)</u>	<u>100ft²(kg/m²)</u>	<u>100ft²(kg/m²)</u>
5	9	42 (20.6)	15 (7.4)	19 (9.3)
	10	56 (27.4)	22 (10.8)	27 (13.2)
	11	68 (33.3)	38 (18.6)	46 (22.5)
	12	50 (24.5)	21 (10.3)	26 (12.7)
10	13	50 (24.5)	23 (11.3)	28 (13.7)

Example 14-17

Fluids consisting of 0.41 bbl (65.2 dm³) of diesel oil and 12 pounds (5.4 kg) of gellant clays prepared in Example 2 and 3 in addition to commercial clays 2M2HT/bentonite and BM2HT/bentonite were admixed and stirred for five minutes in a Hamilton Beach mixer at low speed. Fluids consisting of 0.41 bbl (65.2 dm³) of diesel oil, 18 pounds (8.2 kg) asphalt, (Baroid Asphalt, NL Industries, Inc.) and 275 pounds (125 kg) of barite, (Baroid, NL Industries, Inc.) were prepared and admixed with the prepared fluids above to form 350 ml batches which stirred for 15 minutes in a Hamilton Beach mixer.

350 ml samples of Examples 14 to 17 were tested for rheological properties as in Example 5 at 93°F (34°C). The results are presented in Table 4 below.



Table 4

Example No.	Yield Point	10 sec. Gel	10 min. Gel
	lbs/ 100ft ² (kg/m ²)	lbs/ 100ft ² (kg/m ²)	lbs/ 100ft ² (kg/m ²)
5 14	26 (12.7)	7 (3.4)	54 (26.5)
15	30 (14.7)	11 (5.4)	48 (23.5)
16	54 (26.5)	34 (16.7)	74 (36.3)
17	25 (12.3)	11 (5.4)	40 (19.6)

350 ml samples of Examples 14 to 17 were hot rolled at 150°F (65.6°C) for 16 hours. After cooling the batches to 80°F, (27°C) settling of solids were checked prior to measurement of rheological properties as in Example 5 at 93°F (34°C). The results are shown in Table 5 below.

15

Table 5

Example No.	Yield Point	10 sec. Gel	10 min. Gel
	lbs/ 100ft ² (kg/m ²)	lbs/ 100ft ² (kg/m ²)	lbs/ 100ft ² (kg/m ²)
20 14	57 (27.9)	14 (6.9)	73 (35.8)
15	80 (39.2)	38 (18.6)	116 (56.8)
16	91 (44.6)	55 (27)	100 (49)
17	69 (33.8)	39 (19.1)	108 (52.9)

Example 14 shows improved results when mixed in a nonaqueous fluid. These results show improvements in forming a gel quickly and remaining low at 10 minute gel indicating a maintenance of pumpability.

350 samples of Examples 14 to 17 were hot rolled at 150°F (65.6°C) for 16 hours. After cooling the batches to 80°F (27°C), settling of solids were checked prior to measurement of rheological properties as in Example 5 at 93°F (34°C). The results are shown

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in Table 6 below.

Table 6

5	Example No.	Yield Point	10 sec. Gel	10 min. Gel
		lbs/100ft ² (kg/m ²)	lbs/100ft ² (kg/m ²)	lbs/100ft ² (kg/m ²)
	14	85 (41.7)	11 (5.4)	55 (27)
	15	105 (51.5)	31 (15.2)	83 (40.7)
	16	120 (58.8)	45 (22)	82 (40.2)
	17	99 (48.5)	41 (20.1)	78 (38.2)

10

Example 18 - 21

350 ml batches of fluids consisting of 0.69 bbl (110 dm³) of diesel oil, 6 pounds (2.7 kg) emulsifier (EZ mul, NL Industries, Inc.), 0.12 bbl (19.1 dm³) of water, 225 pounds (102.2 kg) of barite, 15 (Bariod, NL Industries, Inc.), 24 pounds (10.9 kg) of calcium chloride and 6 pounds (2.7 kg) of gellant clays EM2HT/bentonite and AM2HT/bentonite prepared in Example 2 and 3 respectively in addition to 2M2HT/bentonite were admixed and stirred for 20 minutes in a Hamilton 20 Beach mixer.

350 ml batch of Examples 18 to 21 were tested for rheological properties as in Example 5 at 88°F (31°C). The results are presented in Table 7 below.

Table 7

Example No.	Gellant Compound	Yield Point	10 sec. Gel		10 min. Gel	
		lbs/100ft ² (kg/m ²)	lbs/100ft ² (kg/m ²)		lbs/100ft ² (kg/m ²)	
5 18	EM2HT/bentonite	9 (4.4)	4 (2.0)		5 (2.5)	
19	AM2HT/bentonite	8 (3.9)	5 (2.5)		6 (2.9)	
20	2M2HT/bentonite	9 (4.4)	5 (2.5)		6 (2.9)	
21	BM2HT/bentonite	8 (3.9)	4 (2.0)		5 (2.5)	

350 ml sample of Example 18 to 21 were hot rolled at 150°F (65.6°C) for 16 hours. After cooling the batches to 80°F, (27°C) settling of solids was checked prior to measurement of rheological properties as in Example 5 at 84°F (29°C). The results are shown in Table 8 below.

Table 8

Example No.	Yield Point	10 sec. Gel		10 min. Gel	
	lbs/100ft ² (kg/m ²)	lbs/100ft ² (kg/m ²)		lbs/100ft ² (kg/m ²)	
18	11 (5.4)	5 (2.5)		8 (3.9)	
20 19	11 (5.4)	5 (2.5)		5 (2.5)	
20	15 (7.4)	8 (3.9)		14 (6.9)	
21	9 (4.4)	4 (2.0)		5 (2.5)	

Mud cake and filtrate were stirred back into the respective samples and the batches were aged for 16 hours at 350°F (177°C).

Each batch was cooled to 80°F (27°C), checked for solids settling and electrical stability. The

(31)

batches were stirred for 5 minutes and tested as with Example 5. HT-HP filtrates were conducted on each batch at 350°F (177°C). The results are shown in Table 9 below.

Table 9

5	Example No.	Yield Point		10 sec. Gel		10 min. Gel	
		lbs/	100ft ² (kg/m ²)	lbs/	100ft ² (kg/m ²)	lbs/	100ft ² (kg/m ²)
	18	8	(3.9)	5	(2.5)	5	(2.5)
	19	10	(4.9)	4	(2.0)	5	(2.5)
	20	12	(5.9)	5	(2.5)	6	(2.9)
10	21	8	(3.9)	4	(2.0)	5	(2.5)

Example 22-27

350 ml batches of packet fluids consisting of 0.63 bbl (100 dm³) of diesel oil, 8 pounds (3.6 kg) emulsifier (Invermul, NL Industries, Inc.), 0.11 bbl (17.5 dm³) of water, 325 pounds (147.5 kg) of Barite, (Baroid, NL Industries, Inc.), 8 pounds filtration aid (Duratone, NL Industries, Inc.), 22 pounds (10 kg) of calcium chloride, 4 pounds (1.8 kg) lime and 9 pounds (4.1 kg) of gellant clays EM2HT/bentonite, AM2HT/ bentonite, and AM2HT/hectorite prepared in Example 2, 3, and 4 respectively in addition to three commercial clays, dimethyl di(hydrogenated-tallow) ammonium chloride, 2M2HT/bentonite; benzyl methyl di(hydrogenated-tallow) ammonium chloride, BM2HT/bentonite, and dimethyl di(hydrogenated-tallow) ammonium chloride, 2M2HT/hectorite were admixed and stirred for 20 minutes in a Hamilton Beach mixer.

350 ml sample of Examples 22 to 27 were tested for rheological properties as in Example 5 at 92°F (33.3°C). The results are presented in Table 10.

Table 10

5	Example No.	Gellant Compound	Yield		10 sec.		10 min.	
			Point		Gel		Gel	
			lbs/		lbs/		lbs/	
			100ft ² (kg/m ²)		100ft ² (kg/m ²)		100ft ² (kg/m ²)	
	22	EM2HT/bentonite	36	(17.6)	11	(5.4)	16	(7.8)
	23	AM2HT/bentonite	42	(20.6)	18	(8.8)	23	(11.3)
10	24	AM2HT/bentonite	55	(27)	23	(11.3)	27	(13.2)
	25	2M2HT/bentonite	60	(29.4)	22	(10.8)	33	(16.2)
	26	BM2HT/bentonite	51	(25)	24	(11.8)	28	(13.7)
	27	BM2HT/hectorite	65	(31.9)	32	(15.7)	39	(19.1)

15 Mud cake and filtrate were stirred back into each batch and the batches were aged at 350°F (176.7°C) for 16 hours. Each batch was cooled to 80°F (27°C), checked for solids settling and electrical stability. The batches were admixed, stirred for 10 minutes and tested as with Example 5 at 90°F (32°C). The results are shown in Table 11 below.

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Table 11

5	Example No.	Yield		10 sec.		10 min.	
		Point		Gel		Gel	
		lbs/		lbs/		lbs/	
		100ft ² (kg/m ²)		100ft ² (kg/m ²)		100ft ² (kg/m ²)	
25	22	20	(9.8)	16	(7.8)	24	(11.8)
	23	28	(13.7)	23	(11.3)	27	(13.2)
	24	31	(15.2)	30	(14.7)	33	(16.2)
	25	34	(16.7)	18	(8.8)	26	(12.7)
	26	26	(12.7)	24	(11.8)	29	(14.2)
30	27	37	(18.1)	28	(13.7)	35	(17.2)

350 ml. batches of Examples 23, 24, 25 and 37 were aged for 16 hours at 300°F (149°C), 400°F (204°C) and 450°F (232°C). The batches were tested as above at 99°F (37°C). and the results are shown in Table 12.

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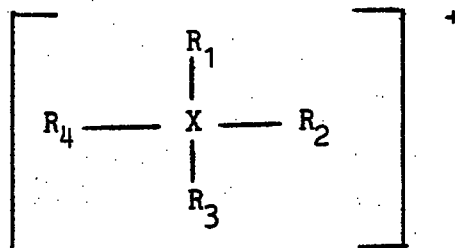
Table 12

Example No.	Temperature °F (°C)	Yield		10 sec.		10 min.	
		Point	lbs/ 100ft ² (kg/m ²)	Gel	lbs/2 100ft ² (kg/m ²)	Gel	lbs/2 100ft ² (kg/m ²)
23	300 (149)	21 (10.3)	21 (10.3)	21 (10.3)	23 (11.3)		
	400 (204)	45 (22.1)	14 (6.7)	14 (6.7)	30 (14.7)		
	450 (232)	13 (6.4)	9 (4.4)	9 (4.4)	16 (7.8)		
24	300 (149)	31 (15.2)	30 (14.7)	30 (14.7)	33 (16.2)		
	400 (204)	150 (73.5)	41 (20.1)	41 (20.1)	57 (27.9)		
	450 (232)	80 (39.2)	22 (10.8)	22 (10.8)	35 (17.2)		
25	300 (149)	38 (18.6)	28 (13.7)	28 (13.7)	37 (18.1)		
	400 (204)	27 (13.2)	11 (5.4)	11 (5.4)	20 (9.8)		
	450 (232)	9 (4.4)	8 (3.9)	8 (3.9)	14 (6.7)		
27	300 (149)	37 (18.1)	28 (13.7)	28 (13.7)	35 (17.2)		
	400 (204)	120 (58.8)	40 (19.6)	40 (19.6)	60 (29.4)		
	450 (232)	40 (19.6)	17 (8.3)	17 (8.3)	30 (14.7)		

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CLAIMS

1. An oil-base fluid comprising an oil phase and from 1 to 50 lbs. per barrel ($2.85 - 143 \text{ kg}/10^3 \text{ dm}^3$) of an organophilic clay gellant comprising the reaction product of an organic cationic compound and a smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of said clay, wherein the organic cation has the formula:



wherein R_1 is selected from a β, γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having 2 to 6 carbon atoms and mixtures thereof; R_2 is a long chain alkyl group having 8 to 60 carbon atoms; R_3 and R_4 are individually selected from a β, γ -unsaturated alkyl group having less than 7 aliphatic carbon atoms, a hydroxyalkyl group having from 2 to 6 carbon atoms, an aralkyl group, an alkyl group having from 1 to 22 carbon atoms and mixtures thereof; X is selected from phosphorus and nitrogen; and wherein the amount of the organic cationic compound is from 90 to 140 milliequivalents per 100 grams of said clay, 100% active clay basis.

2. An oil-base fluid according to claim 1, wherein the organophilic clay gellant is present in an amount of from 1 to 10 lbs per barrel ($2.85 - 28.6 \text{ kg}/10^3 \text{ dm}^3$) of fluid.



3. An oil-base fluid according to claim 1, wherein the organophilic clay gellant is present in an amount of from 6 to 50 lbs per barrel (17.1 - 143 kg/10³dm³) of fluid.
4. An oil-base fluid according to any one of claims 1 to 3, wherein the smectite-type clay is selected from hectorite and sodium bentonite.
5. An oil-base fluid according to any one of claims 1 to 4, wherein the group R₁ in the organic cation is a β , γ -unsubstituted group selected from cyclic groups, acyclic alkyl groups having less than 7 carbon atoms, acyclic alkyl groups substituted with aromatic groups, aromatic groups substituted with aliphatic groups and mixtures thereof.
6. An oil-base fluid according to any one of claims 1 to 4, wherein the group R₁ in the organic cation is a hydroxyalkyl group having from 2 to 6 carbon atoms selected from hydroxyl substituted cycloalkyl groups and hydroxylsubstituted acyclic alkyl groups, and mixtures thereof.
7. An oil-base fluid according to any one of claims 1 to 6, wherein the group R₂ in the organic cation has from 12 to 22 carbon atoms.
8. An oil-base fluid according to claim 7, wherein the group R₂ is a long chain fatty acid group.
9. An oil-base fluid according to any one of claims 1 to 8, wherein the amount of the organic cationic compound is in the range of from 100 to 130 milliequivalents per 100 g of the clay, 100% active clay basis.
10. An oil-base fluid according to any one of claims 1 to 9, which additionally comprises a dispersed aqueous phase comprising from 2 to 50% by volume of water.
11. An oil-base fluid according to claim 10, which additionally comprises a water-in-oil emulsifier.



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12. An oil-base fluid according to claim 11, wherein the emulsifier is present in an amount of from 1 to 30 lbs per barrel ($2.85 - 85.7 \text{ kg}/10^3 \text{ dm}^3$) of the fluid.
 13. An oil-base fluid according to any one of claims 1 to 9, wherein the fluid is non-aqueous.
 14. A method of insulating casing in a wellbore which comprises pumping an oil-base fluid according to any one of claims 3 to 13 into an annular space within the wellbore and thereafter gelling the oil-base fluid.
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