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WELL TREATMENT COMPOSITION

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2 Claims. (Cl. 252—8.55)

The invention relates to oil-base fluid compositions having a temporary high viscosity making them especially useful in various methods of treatment of deep wells, such as those drilled for oil and gas.

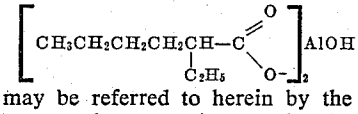
One of the methods of treatment of a deep well in which the composition of the invention find an application involves the so-called fracturing of an earth formation penetrated by a well so as to increase its capacity for fluid flow into or out of the well and thereby increase the output of the well if a producer or increase its receptivity for fluid if the well is for fluid disposal. Such fracturing is usually accomplished by injecting into the well a more or less viscous liquid at a sufficient rate to create in the well hole against the formation to be fractured a pressure exceeding that which the formation can withstand without fracture or rupture. In this way it is believed that cracks and fractures are produced, because, on observing the pressure on the liquid so injected into the well it is found to more or less suddenly decline during the injection after the pressure has reached one which is calculated to be sufficient to overcome the resistance of the earth formation to the rapid inflow of fluid. Following or during such a relatively high pressure injection, a particulated solid material, such as sand, usually also is carried into the earth formation so as to deposit fluid permeable masses of solid particles in the cracks, fractures, or other openings produced by the injection. For conveying such particulated solid material into the well formations, more or less viscous fluid media are preferably used.

Various difficulties arise with the fluids heretofore used in such operations which leave much to be desired. One of the difficulties is that if the liquid or fluid is thin enough to be readily pumped and injected into the well hole, it may drain away or seep into the earth formation without exerting in the well hole as high a pressure as desired. On the other hand if the fluid be made thick enough so that it strongly resists penetration into the earth, and thereby allows high pressure to be exerted in the well hole without excessive seepage, the fluid is difficult to pump and transmit through the well bore to the face of the formation to be treated. Still another difficulty is that fluids, which may be thick enough to penetrate the earth only under high pressures, do not return readily to the well hole when the injection pressure is released. In such circumstances, the fluid permeability of the earth formation may be adversely affected instead of being benefited from a fracturing operation. Although it has been proposed to inject into the earth formation diluents or gel breakers after an injection of a thick oil-base fluid, such as a gelled gasoline, following a fracturing operation, such injections cannot be depended upon always to reach and mingle with the thickened fluid because of the limited space available in the interstices of the earth for mingling to occur. Similar difficulties arise on attempting to use thick liquids for conveying a particulated solid material into the fractures or cracks in the earth formation of the well.

Accordingly, it is an object of the invention to provide a fluid composition which is initially easily conveyed through the well tubing or casing, as the case may be, and attains in the well hole after a time a gelled state in which it can be injected into the earth but only by applying high pressure yet, in spite of its low formation-penetrating characteristics, spontaneously thins after a predeterminable time, the thinning being assisted by oil or brine, thereby allowing it to be returned to the well hole from the earth formation by the fluid therefrom produced.

Other objects and advantages will appear as the description of the invention proceeds.

The composition contemplated by the invention and attaining the foregoing and related objects comprises a petroleum fraction which is liquid at ordinary temperatures, such as kerosene, diesel fuel, and distillate. To the petroleum fraction is added a thickening agent, consisting of the aluminum salt of 2-ethyl hexoic acid having the formula:



This salt may be referred to herein by the short term aluminum octoate for convenience. The aluminum octoate brings about a more or less partial gelling of the petroleum fraction upon the addition of a suitable catalytic agent referred to as a thickening controlling agent as later explained.

The amount of the aluminum octoate to use may be determined by trial in accordance with the amount of thickening to be produced as hereinafter explained. In general the amount of the aluminum octoate may range from about 10 to 90 pounds per 100 gallons of the petroleum fraction.

The aluminum octoate is dispersed in the petroleum fraction in any suitable manner as for example by means of a motor driven agitator operating in a tank in which the petroleum fraction and aluminum octoate are placed for mixing.

Into the dispersion so-obtained, there is dispersed, as by a similar mixing operation, an agent herein referred to as a thickening controlling agent and designated TCA for short. The TCA used in one having the property of causing the aluminum octoate to thicken the liquid petroleum fraction at ordinary temperature and subsequently to bring about at least partial thinning of the so-thickened or more or less gelled petroleum fraction. The TCA accelerates both thickening and thinning of the liquid petroleum fraction to an extent which permits it to become thickened and to remain in a thickened condition for a predeterminable time depending upon the amount and kind of TCA used.

As a TCA there may be used various petroleum oil-soluble organic chemical compounds or mixtures of them having a generally low dissociation constant, as for example, organic acids and bases and their petroleum oil-soluble salts having dissociation constants of about 1×10^{-3} to 1×10^{-15} or preferably between 10^{-4} and 10^{-12}. It is advantageous to use together at least two such agents having different dissociation constants as this results in obtaining a better thinning effect than is obtainable usually with but one such agent without adversely affecting thickening of the liquid petroleum fraction. Examples of suitable TCA's are: oleic acid, linoleic acid, p-toluidine, ammonium stearate, dinonyl phenol, di-2-ethyl hexylamine acetate, and nonyl phenol.

The thickening controlling agent (TCA) may be used in an amount between 0.15 to 9.4 percent of the weight of the petroleum fraction depending upon the rate and extent of thickening desired. In general from about 0.2

to 4.5 percent by weight of the petroleum fraction suffices for most purposes.

As soon as a TCA is dispersed in the liquid petroleum fraction in which the aluminum octoate is dispersed thickening commences and at a rate which depends upon the amount and kind used. The viscosities attained may exceed 100,000 centipoises (cps.). Viscosities up to 100,000 cps. may be measured by means of the Brookfield synchro-electric viscosimeter. Viscosities beyond 100,000 cps. may be measured by determining the rate of flow of the thickened petroleum fraction through a straight tube 2 inches long having a cylindrical bore of 3/16 inch in diameter. In making a viscosity measurement with the tube the material to be measured is forced through the tube under a pressure of 2 pounds per square inch and the time in seconds required for one gram of the material to pass through the tube, multiplied by the factor 9000, is taken as the relative viscosity of the material in jel viscosity units (herein abbreviated JVU). A liquid having a viscosity in cps. of 100,000, as measured by the Brookfield synchro-electric viscosimeter, will have a viscosity of 100,000 JVU on being subject to a viscosity measurement by means of the tube just described.

The rate at which thickening occurs varies with the kind of TCA used and roughly is more rapid the higher the dissociation constant of the agent. This is illustrated by the data of Table I. The data of Table I are derived from tests in which 3 grams of aluminum octoate were dispersed in each of 7 batches of 100 ml. of kerosene at 80° F. The time required for the resulting mixtures to thicken to 10,000 cps. was observed after dispersing in the mixtures various phenolic thickening controlling agents (TCA) as noted in the table.

TABLE I

Batch No.	TCA	Amount TCA, percent	Minutes to reach viscosity of 10,000 cps. at 80° F.
1	chlorophenol	1	less than 5
2	phenol	1	5
3	metacresol	1	10
4	do	0.4	48
5	orthocresol	0.4	60
6	nonylphenol	1.0	40
7	dinonylphenol	1.0	120

As illustrative of the effect on viscosity of the TCA in a dispersion of aluminum octoate in kerosene, the following data in Table II are cited. In obtaining these data, three batches of 100 ml. of kerosene and 3.5 grams of aluminum octoate were prepared by dispersing the octoate in the kerosene. As a TCA, into one of the batches was dispersed 0.9 ml. of oleic acid and into another 1.4 ml. The third batch, with no TCA, served as a blank for comparison. The viscosity of each batch was measured by the tube method described above at various time intervals after preparation as shown in the table.

TABLE II

Time vs. viscosity,[1] 100° F.

Minutes after preparation	TCA added		
	Batch 1—0.9 ml.	Batch 2—1.4 ml.	Batch 3—0
	JVU	*JVU*	*Cps.*
10	675,000	900,000	6
20	700,000	800,000	6
45	650,000	775,000	6
60	625,000	725,000	7
90	600,000	650,000	8
180	575,000	600,000	100
600	400,000	425,000	1,000

[1] Viscosities below 100,000 are in cps., higher viscosities are in JVU's.

From the foregoing data, it is manifest that the aluminum octoate-thickened petroleum liquid becomes highly viscous but gradually thins as it ages. Still further thinning takes place when crude oil mixes with and dilutes the thickened material as in an earth formation yielding crude oil.

Thinning after thickening is also accelerated by the use of a more highly dissociated TCA along with a TCA which is less dissociated. For example, acetic acid with a dissociation constant of 1.75×10^{-5} at 25° C. shows a marked tendency to bring about thinning after thickening has occurred. Similar effects are observed with butyric acid, potassium oleate, butyl amine, and octadecyl amine acetate, for example. This thinning effect is illustrated in the data tabulated in Table III for three batches each of 100 ml. of kerosene thickened with 2 grams of aluminum octoate and containing 1 ml. of oleic acid. To one of the batches 0.04 ml. of acetic acid was added, to a second batch 0.08 ml. was added and to a third batch 0.12 ml. of acetic acid added.

TABLE III

Time vs. viscosity,[1] thinning effect of acetic acid, 100° F.

[Acetic acid added]

Hours after preparation	Batch 1—0.04 ml.	Batch 2—0.08 ml.	Batch 3—0.12 ml.
½		105,000	60,000
1	57,000	260,000	57,000
2	650,000	260,000	34,000
4	750,000	105,000	15,000
6	700,000	45,000	8,000

[1] Viscosities below 100,000 are in cps., higher viscosities are in JVU's.

Inasmuch as the mixture of aluminum octoate and petroleum liquid thickens more or less rapidly after adding a TCA, the operation of the introduction of the mixture into the well, and into the earth formation, if desired, is completed before the mixture becomes too thick to pump, as when the viscosity reaches about 25,000 cps. By using an amount of TCA which promotes the desired extent of thickening followed by thinning and having regard to the rate at which the mixture thickens, the time interval before the mixture becomes too thick to pump can be made as long as needed to make the injection into the well and also into the adjacent earth, if desired. In ascertaining the amount of TCA to use, the temperature is taken into account as the rate of thickening increases with increase of temperature. The effect of temperature on the rate at which mixtures of aluminum octoate and a liquid petroleum fraction thicken to a viscosity of 10,000 cps., for example, is illustrated by the data tabulated in Table IV in which 100 ml. batches of kerosene containing 3 grams of aluminum octoate were thickened at different temperatures with various amounts of a TCA composed of 96 parts of oleic acid and 4 parts of acetic acid.

TABLE IV

Time vs. temperature to reach viscosity of 10,000 cps.

Ml. TCA[1]	Minutes elapsed in reaching viscosity of 10,000 cps.		
	at 80° F.	at 100° F.	at 120° F.
2.25	12	4	
1.5	31	7	4
0.75	105	25	10
0.3			39

[1] Composed of 96 parts of oleic and 4 parts of acetic acid by volume.

From the data of Table IV, it is evident that by either

decreasing the amount of TCA or the temperature of operation the time available for handling the mixture before its viscosity exceeds 10,000 cps. is lengthened.

The maximum viscosities attained in a series of equal thickening times at various temperatures for various proportions of the aluminum octoate and the TCA are shown in Table V, in which the TCA is a mixture of 96 parts of oleic and 4 parts of acetic acid by volume, and in table VI, in which the TCA is a mixture of 99 parts of oleic and 1 part of acetic acid by volume.

TABLE V

Viscosity vs. temperature and concentration of aluminum octoate and TCA [1] for the same thickening time at 80° F. to 150° F.

Grams Al Octoate per 100 ml. Kerosene	Viscosities vs. ml. TCA per gram of Al Octoate		
	37 minutes [2]	31 minutes [2]	13 minutes [2]
	80° F., 1.0 ml.	105° F., 0.8 ml.	150° F., 0.4 ml.
1.5	80,000 cps.		
2.0	135,000 JVU.	100,000 cps.	70,000 cps.
2.25	225,000 JVU.	150,000 JVU.	90,000 cps.
2.5	450,000 JVU.	325,000 JVU.	110,000 JVU.
2.75	975,000 JVU.	700,000 JVU.	175,000 JVU.
3.0		1,000,000 JVU.	325,000 JVU.
3.25			600,000 JVU.
3.0			1,000,000 JVU.

[1] 96 parts of oleic and 4 parts of acetic acid by volume.
[2] Time taken to attain the viscosity listed which is the maximum attained.

TABLE VI

Viscosity vs. temperature and concentration of aluminum octoate and TCA [1] for the same thickening time at 200° F. to 300° F.

Grams Al Octoate per 100 ml. Kerosene	Viscosities vs. ml. TCA per gram of Al Octoate		
	8 minutes [2]	5.3 minutes [2]	3.3 minutes [2]
	200° F. 0.35 ml.	250° F. 0.20 ml.	300° F. 0.15 ml.
3.0	150,000 JVU.	110,000 JVU.	50,000 cps.
3.5	300,000 JVU.	200,000 JVU.	100,000 cps.
4.0	475,000 JVU.	350,000 JVU.	175,000 JVU.
4.5	750,000 JVU.	500,000 JVU.	250,000 JVU.
5.0	1,200,000 JVU.	750,000 JVU.	375,000 JVU.
5.5		1,100,000 JVU.	550,000 JVU.
6.0			750,000 JVU.

[1] 99 parts of oleic and 1 part of acetic acid by volume.
[2] Time taken to attain the viscosity listed which is the maximum attained.

In some instances, as when it is desired to use the aluminum octoate-thickened liquid petroleum fraction as a fluid medium with which to convey a particulated solid, such as sand, into fractures or cracks and the like in an earth formation, an amount of TCA is used which will induce a sufficient viscosity to be attained to suspend the particles of the particulated solid, yet not too great to be beyond a pumpable stage before injection can be made into the earth. For example sand, 90 percent of which is of 25 to 40 mesh, will settle in an aluminum octoate-thickened petroleum liquid at the rate of 0.3 foot per minute at 80° F. when its viscosity is 260 cps. Such a mixture is readily conveyed by pumping yet the sand remains well suspended during the time required for an injection. The sand falling rate in other mixtures of aluminum octoate-thickened kerosene is shown in the data of Table VII as further examples.

TABLE VII

Volume of Kerosene	Al Octoate, Percent	TCA, ml.	Viscosity, cps., 80° F.	Age [2] in Minutes	Sand [3] Falling Rate in Ft./Min.
100 ml.	0.5	1.0 cresylic acid	2,500	30	0.02
100 ml.	0.3	0.6 cresylic acid	220	30	0.2
100 ml.	0.2	0.4 cresylic acid	20	30	1.8
100 ml.	0.3	0.5 mixture [1]	250	10	0.2

[1] 96 percent by volume of oleic acid and 4 percent by volume of acetic acid.
[2] Age of maximum viscosity.
[3] 30–40 mesh sand.

Contamination by crude oil or brine which may be encountered by the aluminum octoate-thickened petroleum fluid containing a TCA does not unfavorably affect the viscosity changes it undergoes. This is shown by the data in Table VIII. In Table VIII tests of the effect on the rate of thinning are shown, after the thickened mixtures attain their maximum viscosity, of additions of crude oil and brine in the proportions indicated. In these tests, three 100 ml. batches of kerosene were thickened by dispersing therein 2.25 grams of Al octoate followed by 1.8 ml. of TCA consisting of a mixture of 95 percent by volume of oleic acid and 5 percent of acetic acid. Batch 1 was mixed with 10 ml. of crude oil; batch 2 was mixed with 10 ml. of brine; and the third was held as a blank for comparison. All three batches were aged at 100° F. and their viscosities measured periodically as indicated in the table after the mixtures attained their maximum viscosities of 160,000 JVU.

TABLE VIII

Mixture under test	Viscosities [1] vs. time at 100° F.			
	initial	5 hours	24 hours	48 hours
1 (added crude oil)	160,000	35,000	18,000	5,000
2 (added brine)	160,000	65,000	30,000	30,000
3 (blank)	160,000	140,000	75,000	60,000

[1] Viscosities below 100,000 are in cps., viscosities above 100,000 are in JVU.

Another series of tests similar to those of Table VIII are set forth in Table IX but instead of using 2.25 grams of aluminum oleate the mixtures contain 3.0, and instead of using 1.8 ml. of TCA the mixtures contain 1.2 ml. of the same TCA.

TABLE IX

Mixture under test	Viscosities [1] vs. time at 150° F.			
	initial	5 hours	24 hours	48 hours
1 (added crude oil)	325,000	100,000	5,000	3,000
2 (added brine)	325,000	180,000	75,000	60,000
3 (blank)	325,000	300,000	250,000	1,000,000

[1] Viscosities below 100,000 are in cps., viscosities above 100,000 are in JVU.

On deeply penetrating an oil-bearing formation, the Al octoate thickened oil mixtures containing a TCA become more highly diluted with crude oil and this dilution results in a large reduction in viscosity. Because of the reduction in viscosity resulting from dilution by crude oil in situ, there is no danger of the pores of oil-bearing earth becoming clogged with the mixtures of the invention. The data of the tests of the following Table X illustrate the effect of large dilution by crude oil. In these tests conducted at 100° F., 100 ml. batches of kerosene were thickened with 2.25 grams of Al octoate and 1.8 ml. of a TCA was then added consisting of a mixture of 95 percent by volume of oleic acid and 5 parts of acetic acid. These batches attained a maximum viscosity of 160,000 JVU at 100° F. After attaining

maximum viscosity, various amounts of a crude oil were added to the batches and their viscosities measured periodically thereafter as indicated in Table X.

TABLE X

Ml. crude oil added per 100 ml.	Viscosity, cps.				
	Hours after adding crude oil				
	0	6	20	32	66
20	46,000	38,000	18,000	8,000	4,800
40	26,000	21,000	10,000	3,200	1,800
60	8,000	6,000	4,000	400	210
80	600		78		

By using a combination of two thickening controlling agents having different dissociation constants, the one having the smaller dissociation constant does more to promote thickening than thinning and the one having the higher dissociation constant does more to promote thinning than thickening. As a result better control of the duration of the thickened state may be had. This is a desirable feature of the invention as it permits obtaining a long and controllable time during which the more or less gelled petroleum fraction very strongly resists penetration into earth formations. This property also permits knowing in advance the length of time the petroleum fraction will remain thin before gelling or thickening commences so that the mixture of the petroleum fraction, aluminum octoate, and TCA may be introduced into a well bore and more or less deeply into the adjacent earth before the mixture becomes too thick to be readily pumped. Thickening thereafter may take place in the interstices of the earth formation away from the well hole thereby producing a temporary plugging effect beyond the well hole wall. Subsequently a liquid such as oil, water or brine may be injected under a suitable pressure to produce fractures deeply in the earth since the temporary plugging of the surrounding earth by the more or less gelled petroleum fluid confines the fracturing liquid to the regions in the formation adjacent to the gel.

Various advantages accrue to the invention in addition to those already mentioned. The composition may be used for example in connection with perforating well casing in wells in which it is necessary to maintain hydrostatic control as by a column of drilling mud. In such wells, it is desirable to prevent the drilling mud from penetrating and permeating the formation following the perforation operation. By displacing the drilling mud with the composition of the invention from that portion of the casing to be perforated and conducting the perforating operation through the composition after it is allowed to thicken, the drilling mud will be prevented from passing into the formation through the perforations thus made and contaminating the formation. After a time the composition thins permitting its removal from the well along with the drilling mud.

The composition may be used advantageously in general in all cases where it is desirable to protect an earth formation from fluid intrusion from a well hole, as for example in acidizing a plurality of formations one at a time from the same well hole.

While many of the examples of the invention involve the use of mixtures of oleic acid and acetic acid as a thickening controlling agent, it is to be understood that other mixtures of oil-soluble organic compounds may be used similarly having dissociation constants within the aforesaid limits. Slower rates of thickening, where desired, may be achieved by the use of mixtures of nonyl phenol and glacial acetic acid. Such mixtures also have the advantage of maintaining the thickened petroleum fraction at a high viscosity for a longer time before a breaking down or thinning of the gelled state occurs. For example, a mixture of 92.5 percent of nonyl phenol and 7.5 percent of glacial acetic acid by volume permits viscosities to be attained of up to 1,000,000 JVU. But before these viscosities are attained from 4 to 16 hours may elapse, at temperatures of 80° to 170° F., during which the composition may be pumped or otherwise deposited in the well hole.

This application is a division of our copending application Serial No. 434,072, filed June 2, 1954, on which Patent No. 2,794,779 issued June 4, 1957.

We claim:

1. A fluid composition having a temporary high viscosity comprising a base of a liquid petroleum fraction, said base having dispersed therein as a thickening agent aluminum octoate and a thickening controlling agent consisting of a mixture of acetic acid and a phenolic compound selected from the group consisting of chlorophenol, phenol, metacresol, orthocresol, nonyl phenol, dinonyl phenol, the aluminum octoate being present in amount between 10 and 90 pounds per 100 gallons of the liquid petroleum fraction and the thickening controlling agent being present in amount between 0.15 and 9.4 percent of the weight of the petroleum fraction, the amount of the acetic acid being from 0.04 to 0.12 ml. per 100 ml. of the petroleum fraction, said thickening controlling agent causing the composition to thicken and thereafter to thin.

2. A composition according to claim 1 in which the phenolic compound is nonyl phenol.

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