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2,802,531

WELL TREATMENT

Paul H. Cardwell, Midland, Mich., and Louis H. Eilers and Arthur Park, Tulsa, Okla., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

No Drawing. Application April 26, 1954,
Serial No. 425,758

6 Claims. (Cl. 166—42)

The invention relates to the treatment of wells especially those drilled for oil or gas. More particularly, the invention relates to methods of facilitating the flow of fluid in an earth formation penetrated by the bore of a well by the injection into the formation through the well bore of liquid carrying in suspension particulated solids.

Among the methods in current use for facilitating flow of fluid either into or out of earth formations penetrated by the bore of a well are those involving liquid injections into the earth through the well bore at hydrostatic pressures great enough to form channels or passageways by fracturing or parting the earth formations into which the liquid is injected. In such injections, the pressures used are oftentimes greater than those required to lift the overburden of earth and at least great enough to exceed the bonding strength of the formations encountered. While it is apparent that fractures or cracks may be formed in oil- or gas-bearing formations by the hydraulic action described, as a result of which the facility with which oil or gas flows to the well may be increased, the difficulty may arise that on releasing the pressure on the injected liquid used to create the fractures or cracks these tend to close due to the weight of the overburden. As a consequence, it is generally the practice during fracturing to convey into the earth a particulated hard solid material, such as sand in suspension in the fracturing medium. The particulated solids on being carried into the fractures or cracks formed by the high pressure hydraulic action described, act as props and hold open the fractures and cracks after the injection pressure is released. But certain disadvantages inure to this practice which limits its usefulness. Among these are that the particulated solids comprising the propping agent do not remain suspended in the liquid media conventionally used to convey the solids into the earth formation. These media are hydrocarbon liquids, such as gasoline, kerosene, crude oil, and the like, generally rendered more viscous by dissolving therein a thickening agent, such as soap. As a consequence of the tendency for the particulated solids to settle in all such conveying media, special mixing facilities must be provided at the well site to mix, and maintain in suspension, the particulated solids in the conveying medium while making the injection into the well. The thickened or viscous oils oftentimes conventionally used have the added disadvantage that they are difficult to pump through the well tubing and do not return from the earth formation after their injection so that an especial treatment of the earth formation is required to purge it of the injected liquid. Still another disadvantage is that, if, during an injection into the well of the conventional mixture of conveying liquid and particulated solid, it should become necessary to stop the injection, settling out of the propping agent occurs in the injection pump and piping connecting the pump with the well and in the well bore or well tubing, if such be used, making it difficult, if not impossible, to restart the injection operation.

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Accordingly, it is an object of the invention to provide an improved method of treating earth formations penetrated by the bore of a well so as to facilitate flow of fluid into or out of the earth formation involving the conveying of particulated solids, e. g. sand, through the well into the earth formation, whereby the foregoing disadvantages are overcome. Other objects and advantages will become apparent as the description of the invention proceeds.

The invention is predicated upon forming a pumpable fluid emulsion, comprising immiscible liquids, mixing therewith a suitable particulated solid material, and then injecting the resulting mixture into the earth formation through the well. The particles of the solid material or propping agent are entrained in the emulsion at the interface between the particles of the liquid phases of the emulsion and thereby are held in substantially permanent suspension without the need for continuous agitation during injection. The emulsion mixture is easily pumped and either readily penetrates permeable earth formation or can be forced into the earth by the application of sufficient pressure. On passing into the earth formation, the emulsion spontaneously breaks thereby releasing the particles of propping agent which become lodged in the fractures or cracks of the formation into which the injection is made. The solid particles so-deposited form fluid permeable masses which hold apart the walls of the fractures, permit the return to the well hole of the emulsion liquids without returning the solid particles when the injection pressure is released, and facilitate oil flow either out of or into the formation.

In carrying out the invention at least two immiscible liquids are emulsified together in the presence of a suitable emulsifying agent, that is, one such that the emulsion obtained is capable of being injected into the interstices of an earth formation under moderate pressure and of spontaneously therein breaking. In this way, relatively low pumping pressures suffice to make the injection, and, deposition in the earth formation of the particulated solids carried into the formation by the emulsion is assured when the emulsion breaks. Suitable emulsions are obtained when one of the immiscible liquids involved constitutes the major portion of the emulsion. Proportions of near equal parts of each immiscible liquid are generally to be avoided. In other words, one of the liquids, exclusive of the emulsifying agent, should constitute substantially more than half of the emulsion, e. g. from about 55 to 98.5 percent by volume or preferably from about 66 to 97 percent of the emulsion.

For reasons of cheapness and availability, one of the liquids is preferably aqueous and may be any ground water either potable, saline, alkaline or acid, the purity of the water used apparently not being critical. A wide variety of liquids which are immiscible with the aqueous liquids are available. For example, there may be used petroleum oil, such as crude oil, petroleum fractions, such as refined oil, kerosene, gasoline, diesel oil, fuel oil, and the like, or other water immiscible hydrocarbon liquid, such as benzene, styrene, xylene, toluene, and the like.

If, in employing an aqueous liquid, it be acidified, the further advantage is realized of dissolving acid-soluble material in the earth formation and producing pore enlargement as a result. In addition, there is obtained a quick demulsification of the emulsion as its acid component becomes neutralized in the earth formation, thereby allowing the well to be put into production as soon after the injection as the necessary changes in piping at the well head can be arranged. For example, in an emulsion of dilute hydrochloric acid in oil containing an admixture of 1.5 pounds of 20 to 40 mesh Ottawa sand per gallon, the sand does not noticeably settle in an hour but by

contacting the mixture of the emulsion and sand with either earth formation material containing acid-soluble matter or fine sand the emulsion loses its ability to keep the Ottawa sand in suspension and the Ottawa sand settles at the rate of at least 2000 inches per hour. In formulating emulsions using an acidified aqueous solution as one of the immiscible liquids, ordinary aqueous hydrochloric acid may be used such as that containing from about 2 to 25 percent of HCl by weight, although other concentrations may be used. A preferred concentration of the HCl is about 15 percent.

As illustrative of suitable emulsifying agents, the following types are cited with examples: (1) long chain carboxylic acids, e. g. butyric acid, valeric acid, palmitic acid, stearic acid, mellisic acid, undecylenic acid, oleic acid, ricinoleic acid, euricic acid, abietic acid, dammarolic acid, sebacic acid; (2) long chain alcohol hydrogen sulfates having from 9 to 31 carbon atoms, e. g. nonyl alcohol hydrogen sulfate, lauryl alcohol hydrogen sulfate, diamyl phenoxyethanol hydrogen sulfate, myricylalcohol hydrogen sulfate, 3,9-diethyl tridecanol-6 hydrogen sulfate; (3) alkyl aryl sulfonic acids having 8 to 20 carbon atoms in the alkyl group and 6 to 10 carbon atoms in the aryl group, e. g. diamyl benzene sulfonic acid, triamyl benzene sulfonic acid, diamyl naphthalene sulfonic acid, dinonyl phenol sulfonic acid, dodecyl phenol sulfonic acid, pentadecyl resorcinol sulfonic acid, nonyl phenol sulfonic acid; (4) long chain amides, e. g. octadecyl amide, trioleyl amide of diethylene triamine, n-capramide, n-lauramide, n-stearamide, N,n-octadecyl stearamide, N,N-di-n-octadecyl stearamide, N-n-dodecyl lauramide, N-n-octadecyl phthalamide; (5) long chain polyamides, such as the product formed by reacting together: (a) 1 mole of dilinoleic acid and 1 mole of ethylene diamine, (b) 1½ moles of dilinoleic acid and 1 mole of diethylene triamine, (c) 2 moles of dilinoleic acid and 1 mole of triethylene tetraamine, (d) 3 moles of oleic acid and 1 mole of diethylene triamine, (e) 1 mole of oxalic acid and 2 moles of octadecyl amine, (f) 5 moles of stearic acid and 1 mole of tetraethylene pentamine, (g) 3 moles of euricic acid and 1 mole of diethylene triamine, (h) 3 moles of hexadecyl amine and 1 mole of aconitic acid (i) 1 mole of dilinoleic acid and 2 moles of ethanolamine, (j) 1 mole of dilinoleic acid and 1 mole of hydroxyethyl ethylene diamine; (6) hydrochlorides of long chain amines, e. g. dioctyldecyl amine, dihexyl amine, octadecyl amine, n-hexadecyl amine, n-octadecyl amine, oleic amine, rosin amine (19 carbon atoms), di-n-hexylamine, di-n-octyl amine, di-n-octadecyl amine, dicyclohexylamine, dibenzyl amine, tri-n-octadecyl amine; (7) condensation products of ethylene oxide with amines having a chain length of 12 to 20 carbon atoms, e. g. the condensation product of 1 mole of rosin amine and 11 moles of ethylene oxide; (8) condensation products of ethylene oxide with alkyl phenols in which the alkyl group contains 8 to 18 carbon atoms, e. g. the condensation product of 1 mole of dodecyl phenol with 12 moles of ethylene oxide; (9) condensation products of ethylene oxide with organic acids and fatty acids; (10) ester polyether alcohol, such as the condensation product of sorbitan oleate with 12 moles of ethylene oxide; (11) alkyl aryl benzene polyether sulfates, e. g. the sulfate of the condensation product of 1 mole of para-iso-octyl phenol with 50 moles of ethylene oxide; (12) quaternary ammonium salts of the type $R_2N(CH_3)_2x$, wherein R is a hydrocarbon radical having from 8 to 18 carbons and x is a halide salt, e. g. didodecyl dimethyl ammonium chloride.

Emulsions in which the aqueous phase is the external or continuous phase and an oil or oily liquid is the internal or dispersed phase result from a suitable choice of emulsifier capable of stabilizing such emulsions. As an example, there may be used the reaction products obtained by reacting together ethylene oxide and a polyglycol.

In making the emulsion, the emulsifier is preferably first mixed with the liquid in which it most readily disperses or dissolves, this liquid being the one which usually

constitutes less than half of the volume of the emulsion. Emulsification of the liquids is effected in any of the ways known in the art of making emulsions. A generally satisfactory method is to stir together vigorously the liquids to be emulsified in the presence of an emulsifying agent, and, at the same time recirculate the resulting mixture. Recirculation may be accomplished by withdrawing the stirred mixture from the mixing zone and pumping it back by means of a force pump through a small orifice, e. g. one having an opening $\frac{3}{16}$ inch in diameter.

The suitability of any given emulsifying agent for the purpose of the invention is best ascertained by trial as it is necessary to produce an emulsion having sufficient stability to remain unbroken for considerable periods of time and in some instances at moderately elevated temperatures, such as those encountered in deep wells. It is desirable, therefore, for the emulsion to remain unbroken for as long as 30 minutes more or less, for example, and preferably longer in some cases to allow adequate time both for mixing the particulated solid material with the emulsion and for making the injection of the resulting slurry into the earth formation. The emulsion must also be capable of being injected into the earth formation and spontaneously breaking on passing into the interstices of the earth formation as aforesaid. The amount of emulsifying agent required likewise may be ascertained by trial and usually ranges from about 0.5 to 12 percent of the combined weight of the liquids to be emulsified.

Preferably as soon as the emulsion is made and the well is ready for treatment, the desired particulated solid material to be conveyed into the earth formation through the well is mixed with the emulsion in suitable proportions in any convenient manner to form a pumpable slurry. The proportions do not appear to be sharply critical and may range, for example, from about 0.5 to 6 pounds per gallon of emulsion. Various solid materials in particulate form may be used which are insoluble in the emulsion as for example, ceramic materials, metals, and rocks. Sand, because of its hardness, cheapness and general availability, is preferred. The particle sizes may vary over a considerable range. The particles should be small enough to pass into the cracks or fractures existing in the formation or produced during the injection treatment but not so small as to exhibit a low fluid permeability when deposited within the earth formation. In general, particle sizes between these extremes are to be used. Generally useful sizes of particles are those which will pass through a No. 20 standard sieve while being retained upon a No. 40 standard sieve. Other sizes may be used such as those between a No. 4 and a No. 120 standard sieve.

In order to assist in delivering the slurry to the particular formation to be treated, a packer may be placed in the well hole or casing, as the case may be, at a suitable depth. The packing means may be either the single or dual variety and set in the well by means of a string of tubing, as understood in the art. In this way, the treating materials to be injected are confined in the well hole adjacent to the formation to be treated and there may be put under sufficient pressure to cause them to enter the formation.

Passage of the slurry, that is, the mixture of particulated solid material and the emulsion, into the earth may be preceded by an injection of a breakdown liquid such as crude oil or other available liquid or by an injection of the emulsion without the particulated solid. The injection of the breakdown liquid is made at rates comparable to those to be employed in injecting the slurry, such as $\frac{1}{2}$ to 5 barrels per minute or more depending upon the capacity of the pumping equipment and the pressures encountered which should not be allowed to exceed the safe working pressures of the well equipment.

During the breakdown injection, the pressure in the well rises, reaches a maximum, and then declines, thereby indicating that rupturing or fracturing of the earth for-

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mation or removal of fluid blocks in the interstices of the earth formation has occurred. In any event, irrespective of the explanation of the causes of the pressure changes during such an injection, the injection of breakdown liquid serves to insure passage into the formation of the slurry subsequently injected. In some instances the breakdown of the formation before injecting the slurry may be omitted. In such instances, it is usual for the injection pressure to pass through a maximum as in the case of the injection of a breakdown liquid. Omission of the injection of the breakdown liquid ahead of the slurry is not advisable where there is the possibility of the particulated solid becoming separated from the emulsion at the face of the formation as by filtration. It has been found that by preceding the slurry injection with an injection of oil or other breakdown liquid, as aforesaid, at rates producing a breakdown of the formation as evidenced by a change from a rising to a declining pressure occurring during the injection (without substantially changing the injection rate) the risk of the particulated solid material filtering out of the slurry at the face of the formation is reduced, if not eliminated.

The volumes of breakdown liquid and slurry to use varies widely with different earth formations and are best determined by experience using as a guide at least the amount required to produce a breakdown pressure at nominal injection rates. For example, it is a common experience in making such injections, say at about 2.5 barrels per minute, to observe a rise in the injection pressure during the initial stages of the injection and to observe a leveling off in pressure after 3 to 20 barrels of liquid has been injected. The leveling off in pressure is usually followed by a more or less sudden decline in pressure as though a break-through of the passage of liquid into the formation has taken place which permits a higher injection rate without a pressure increase.

After a breakdown of the formation is obtained, the slurry may be injected readily in an amount which is preferably at least as large as, if not larger than, the volume of liquid required to reach a breakdown pressure. For example, volumes of slurry of from 1000 to 30,000 gallons have been used effectively. It is to be understood however that the injection of the slurry sometimes can be made without attaining a breakdown pressure either before or during the slurry injection nevertheless injection is facilitated by introducing slurry-free liquid into the well ahead of the slurry as aforesaid.

The following examples are illustrative of the practice of the invention:

Example 1

A well having a depth of 1420 feet in the Cross Cut sand formation in Brown County, Texas, equipped with tubing and casing was treated by injecting into the producing formation through the casing perforations, extending between 1392 and 1394 feet, 1000 gallons of a slurry consisting of an oil-water emulsion containing in suspension 500 pounds of 20-40 mesh sand and 500 pounds of 40-60 mesh sand, the slurry being preceded by an injection of a breakdown liquid. The emulsion was prepared in a 1000 gallon tank by first placing in it 35 gallons of water and 4 gallons of emulsifying agent consisting of a 50 percent water solution of the sulfate of the condensation product of 1 mole of para-iso-octyl phenol with 50 moles of ethylene oxide. These ingredients were stirred to form a uniform mixture whereupon 961 gallons of crude oil were added slowly, about 50 gallons being added per minute during the first two minutes of the addition and then the rate of addition was increased to 100 gallons per minute. Stirring was continued for 5 minutes after all the oil had been added. The resulting emulsion had a viscosity of 610 seconds as determined by a Stormer viscosimeter equipped with an Emil Griner Company Jacob's viscosimeter helical rotor No. G25510C and a weight of 167.61 grams. After preparing the

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emulsion, the sand was stirred into it to form the slurry. In treating this well, crude oil, as a breakdown liquid, was first injected into the formation through the tubing at the rate of about 3 barrels per minute until 27 barrels were injected. During the injection of the oil, the pressure rose to 1100 p. s. i. and decreased to 800 p. s. i., indicating that the formation breakdown pressure was reached with 1100 p. s. i. on the tubing. The oil injection was followed by the slurry of sand and emulsion, prepared as described, which was injected at rates of from 1.5 to 3 barrels per minute and pressures varying from 750 p. s. i. to 1000 p. s. i. The sand-emulsion mixture was followed by a chaser of lease oil which was injected at 700 p. s. i. to clear the well. The pressure on the well was then released whereupon the well began to flow at the rate of 6 barrels of oil per hour. Prior to the treatment, oil would stand in the well to a depth of but 70 feet. Following the treatment, the production at first was a mixture of the components of the broken emulsion and crude oil from the producing formation. After producing the well for a short time, all the emulsion components had been given up while the injected sand remained in the formation.

Example 2

200 pounds of mellisic acid (emulsifying agent) is dispersed in 273 gallons of kerosene, thereby making 300 gallons of kerosene-mellisic acid mixture which is to become the external phase of a water-in-oil type of emulsion. To the mixture so-obtained is added 700 gallons of 5 percent aqueous hydrochloric acid solution containing a conventional amount of a corrosion inhibitor and the resulting mixture is stirred until a thick creamy emulsion is obtained. 800 pounds of sand is then stirred into the emulsion, thereby producing an emulsion-sand slurry which is then ready for injection into an oil well as in treating the producing formations. The injection of the slurry is preceded by an injection of oil to break-down the formation. A chaser of oil is used to displace the slurry from the well into the well's productive formation. After the injection of the slurry into the well's productive formation, the emulsion breaks, thereby depositing the sand from the emulsion in passages in the producing formation. Following the injection, the well is swabbed. The sand remains behind while oil flows freely from the formation into the well.

Example 3

A well, drilled into a sandstone producing formation, is to be treated by making an injection of sand using an emulsion for carrying the sand into the formation. The emulsion is prepared by dispersing 500 pounds of 3,9-diethyl tridecanol-6 hydrogen sulfate in 534 gallons of kerosene and the resulting mixture, having a volume of 600 gallons, is stirred with 1400 gallons of 5 percent aqueous HCl solution until a thick emulsion is obtained in which the acid solution is the dispersed phase. It has a volume of 2000 gallons. 2000 pounds of sand is uniformly dispersed in the emulsion by stirring the emulsion while adding the sand and the resulting slurry is then ready for use in the well. In preparing the well for treatment, a packer is set with the well tubing just above the producing formation and oil is injected into the well through the tubing in amount sufficient to fill the well. The slurry of emulsion and sand is then introduced into the well through the tubing followed by a sufficient volume of oil to displace the mixture from the tubing into the producing formation. The emulsion breaks in the producing formation depositing therein the sand. The well is swabbed following the breaking of the emulsion and put into production.

Example 4

A flowing oil well in a formation similar to that in Example 3 is treated with a mixture of sand and emul-

sion prepared as follows: 93 pounds of dilinoleic acid and 10 pounds of ethylene diamine are heated together at about 200° C. until no more water is evolved. The reaction is complete in 2 hours and yields 100 pounds of polyamide. The polyamide obtained is dispersed in 287 gallons of kerosene, thereby forming 300 gallons of a kerosene mixture containing the polyamide as an emulsifier. To this mixture is added with stirring 700 gallons of 5 percent aqueous HCl, the stirring being continued until a thick emulsion is obtained with the kerosene, the continuous phase. 2000 pounds of sand are then mixed with the emulsion. The resulting slurry has a volume of about 1000 gallons. In making the treatment, a packer is lowered into the well on a string of tubing and set just above the section to be treated and the well is filled with oil. The mixture of sand and emulsion is then injected into the well through the tubing followed by enough oil to displace the mixture out of the well into the adjacent earth plus about 2000 gallons of additional oil. The emulsion breaks in the formation and the injection pressure is released allowing the well to flow.

Example 5

A well in a formation similar to that of Example 3 is treated in similar manner with a mixture of sand and an emulsion prepared as follows: 17 pounds of diethylene triamine and 137 pounds of dilinoleic acid are heated together at about 200° C. until no more water is evolved. The reaction involved is complete in two hours yielding 150 pounds of a polyamide as an emulsifying agent. The polyamide thus obtained is dispersed in 230 gallons of kerosene making 250 gallons of kerosene-polyamide mixture which is emulsified with 750 gallons of 15 percent aqueous HCl by stirring. 1000 gallons of emulsion is obtained in which the acid solution is the dispersed phase. Into the emulsion is dispersed 3000 pounds of sand and the resulting slurry of sand and emulsion is injected to the well in a similar manner to that of Example 3.

Example 6

A well in a formation similar to that in Example 3 is treated with a mixture of sand and an emulsion prepared as follows: 20 pounds of ethylene diamine and 186 pounds of oleic acid are heated together at about 250° C. until no more water is evolved. This operation is complete in 2 hours. The resulting diamide weighing about 200 pounds is suspended in 273 gallons of kerosene and the resulting suspension is emulsified by mixing it with 700 gallons of 10 percent aqueous hydrochloric acid solution containing a small amount of corrosion inhibitor. The thick emulsion which is obtained is mixed with sand in the desired amount to form a slurry. Oil is injected into the formation and then the slurry is injected into the earth formation. The slurry is followed by an injection of oil to clear the well. The well is then put into production.

Example 7

A well in a formation similar to that of Example 3 is treated with a mixture of sand and an emulsion made as follows: 15 pounds of oxalic acid and 88 pounds of octadecylamine are heated together at about 200° C. until no more water is evolved. This operation requires about 2 hours. As a result, there is obtained about 100 pounds of polyamide which is suspended in 287 gallons of kerosene to make 300 gallons of kerosene-polyamide mixture. The mixture so-obtained is stirred while adding to it 700 gallons of 5 percent aqueous HCl, thereby making 1000 gallons of thick emulsion. Sand is mixed with the emulsion so-obtained and the resulting mixture is injected into the producing formation of the well. The mixture is followed by a chaser of crude oil and then the well is put into production.

Example 8

A well is drilled to a depth of 7300 feet in the Spraberry sandstone and the bore is cased. The casing is perforated in the interval from 7260 to 7280 feet which is adjacent to the producing formation which is fracture and has a temperature of about 140° F. A string of tubing extends from the casing head into the well to a depth of 7260 feet with a packer set at 7250 feet. This well had a maximum rate of production 2 barrels of oil per hour by swabbing. The well was filled with oil by pumping 47 barrels into the tubing and thereby made ready for the injection of sand slurry which was made as follows: 270 pounds of dioctadecyl amine was dispersed in 564 gallons of kerosene, thereby making 600 gallons of kerosene-amine mixture. To the mixture so-obtained was added while stirring 900 gallons of 5 percent aqueous HCl, the stirring being continued until a thick emulsion was obtained. The resulting emulsion had a volume of 1500 gallons. 1000 pounds of sand was mixed with the emulsion. The slurry obtained was pumped into the well through the tubing behind the oil already pumped in, the rate of pumping being about 2 barrels per minute. The pressure at the tubing head was about 1300 p. s. i. initially and increased to 1800 p. s. i. as the emulsion-sand mixture entered the producing formation and increased further to 2100 p. s. i. while the injection into the producing formation took place. Following the introduction of the emulsion-sand mixture into the tubing, 110 barrels of oil was introduced at the rate of 2 barrels per minute and the pressure at the tubing head declined to 1800 p. s. i. as the oil displaced from the tubing the emulsion-sand mixture. After the oil injection, the well was swabbed three times with a tubing swab which induces the well to flow. The well then flowed returning oil and broken emulsion to the surface leaving the sand in the formation, the rate of production being 28 barrels of oil per hour through a 1/2 inch choke with 250 p. s. i. back pressure on the tubing.

In treating wells, the temperature of which is unusually high, and, for this reason, tend to resolve the emulsions prematurely, as in the well bore before they enter the formation, it is advantageous to use as the emulsifying agent those in group 5 above, that is, the long chain polyamides, although other emulsifiers producing sufficiently stable emulsions may be used.

By a suitable choice of the emulsifying agent emulsions can be prepared which are stable for long periods even though mixed with the particulated solid material and subjected to the elevated temperatures encountered in deep wells. This is illustrated in the following tabulation comparing the stability of the emulsion with and without admixture of sand as the particulated solid material.

Temp., ° F.	Time in hours for emulsion to break	
	No sand present in emulsion	Emulsion mixed with 6 pounds of sand per gallon
80.....	Hours 18	Hours 18
120.....	10	10
150.....	5	5
175.....	1	1

In the tests reported above, the emulsion was prepared by mixing together 96.3 parts of Bartlesville crude oil, 3.5 parts of fresh water, and 0.2 part of an emulsifier consisting of the condensation product of para-iso-octyl phenol with ethylene oxide in the ratio of one mole of para-iso-octyl phenol to 50 moles of ethylene oxide.

The emulsion breaks on being pumped through a core from the earth formation or through a column of sand of 20-40 mesh for example 4 inches long. The emulsions also have a high fluid loss when tested according to the API Code No. 29, second edition, July 1942 (tentative).

For example, it was found that 600 ml. of the emulsion

passed through the filter paper of the API test in 42 seconds.

Where it is desirable to avoid freezing of the emulsion formed with water as one of the immiscible liquids, there may be added to the water a water-soluble alcohol, e. g. ethyl alcohol, in amount sufficient to lower the freezing point of the water to the desired extent. Temperatures as low as -40° F. may be withstood when sufficient alcohol is used.

Among the advantages of the invention are that particulated solid materials, e. g. sand, are readily conveyed in an emulsion as pumpable slurry through either the well casing, tubing string, or open well bore into the desired formations; the injection of the slurry is not seriously impeded by the emulsions as these readily enter fluid permeable earth, particularly when preceded by an injection of oil or other breakdown liquid; the particulated solids are rapidly released from suspension in the conveying media as these lose their emulsified condition in the interstices of the earth formation; because the particulated solids are released from the conveying medium as the slurry permeates the earth formation no further treatment of the earth formation is required following the injection of the slurry and time is saved in putting the well back into production and obtaining pipe line oil.

This application is a continuation-in-part of our co-pending application Serial No. 305,918, filed August 22, 1952, now abandoned.

We claim:

1. The method of treating an earth formation penetrating the bore of a well which comprises forming a slurry of a particulated solid material in a pumpable unstabilized emulsion comprising an aqueous phase and a hydrocarbon oil phase, said emulsion being formed in the presence of an emulsifying agent selected from the group consisting of a water solution of the condensation product of para-iso-octyl phenol and ethylene oxide, the reaction product of diethylene triamine and dilinoleic acid heated together at about 200° C. until no more water is evolved, the reaction product of ethylene diamine and dilinoleic acid heated together at about 200° C. until no more water is evolved, the reaction product of octadecylamine and oxalic acid heated together at about 200° C. until no more water is evolved, and dioctodecylamine, said particulated solid material being substantially insoluble in the emulsion and the size of the particles of the particulated material being capable of passing through a No. 4 standard sieve but not a No. 120 standard sieve, introducing said slurry into the well so as to bring it into contact with the earth formation to be treated and applying pressure upon the slurry in the well sufficient to fracture the earth formation, said particulated solid remaining suspended in the emulsion and said emulsion remaining unresolved until injected into the earth formation and therein breaking to release the particulated solid material from suspension in the emulsion and depositing the particulated solid in the earth formation.

2. The method of treating an earth formation penetrated by the bore of a well which comprises injecting into the earth formation a hydrocarbon liquid at a rate sufficient to produce a breakdown pressure, said injection being continued until after the breakdown pressure is reached, and thereafter injecting into the so-treated formation particulated material suspended in a pumpable unstabilized emulsion comprising an aqueous phase and a hydrocarbon oil phase, said emulsion being formed in the pressure of an emulsifying agent selected from the group consisting of a water solution of the condensation

product of para-iso-octyl phenol and ethylene oxide, the reaction product of diethylene triamine and dilinoleic acid heated together at about 200° C. until no more water is evolved, the reaction product of ethylene diamine and dilinoleic acid heated together at about 200° C. until no more water is evolved, the reaction product of octadecylamine and oxalic acid heated together at about 200° C. until no more water is evolved, and dioctodecylamine, said particulated solid material being substantially insoluble in the emulsion and the size of the particles of the particulated material being capable of passing through a No. 4 standard sieve but not a No. 120 standard sieve, introducing said slurry into the well so as to bring it into contact with the earth formation to be treated and applying pressure upon the slurry in the well sufficient to fracture the earth formation, said particulated solid remaining suspended in the emulsion and said emulsion remaining unresolved until injected into the earth formation and therein breaking to release the particulated solid material from suspension in the emulsion and depositing the particulated solid in the earth formation.

3. The method of treating an earth formation containing acid neutralizing material and penetrated by the bore of a well which comprises forming a slurry of sand and a pumpable unstable emulsion comprising aqueous hydrochloric acid solution emulsified with a hydrocarbon oil in the presence of an emulsifying agent selected from the group consisting of a water solution of the condensation product of para-iso-octyl phenol and ethylene oxide, the reaction product of diethylene triamine and dilinoleic acid heated together at about 200° C. until no more water is evolved, the reaction product of ethylene diamine and dilinoleic acid heated together at about 200° C. until no more water is evolved, the reaction product of octadecylamine and oxalic acid heated together at about 200° C. until no more water is evolved, and dioctodecylamine, said particulated solid material being substantially insoluble in the emulsion and the size of the particles of the particulated material being capable of passing through a No. 4 standard sieve but not a No. 120 standard sieve, introducing said slurry into the well so as to bring it into contact with the earth formation to be treated and applying pressure upon the slurry in the well sufficient to fracture the earth formation, said particulated solid remaining suspended in the emulsion and said emulsion remaining unresolved until injected into the earth formation and therein breaking to release the particulated solid material from suspension in the emulsion and depositing the particulated solid in the earth formation.

4. The method according to claim 1 in which the particulated solid material is sand.

5. The method according to claim 2 in which the particulated solid material is sand.

6. The method according to claim 3 which is preceded by an injection of oil under sufficient pressure to fracture the earth formation.

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