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[54] **METHOD OF DECREASING FRICTION LOSS IN A WELL FRACTURING PROCESS**
14 Claims, 1 Drawing Fig.

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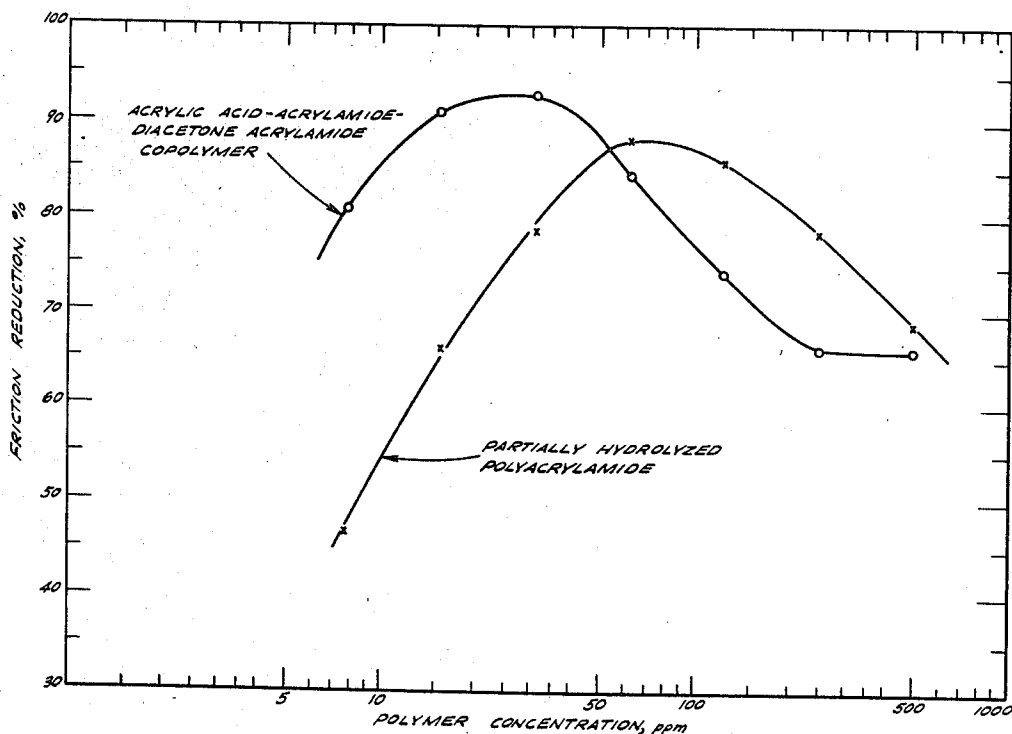
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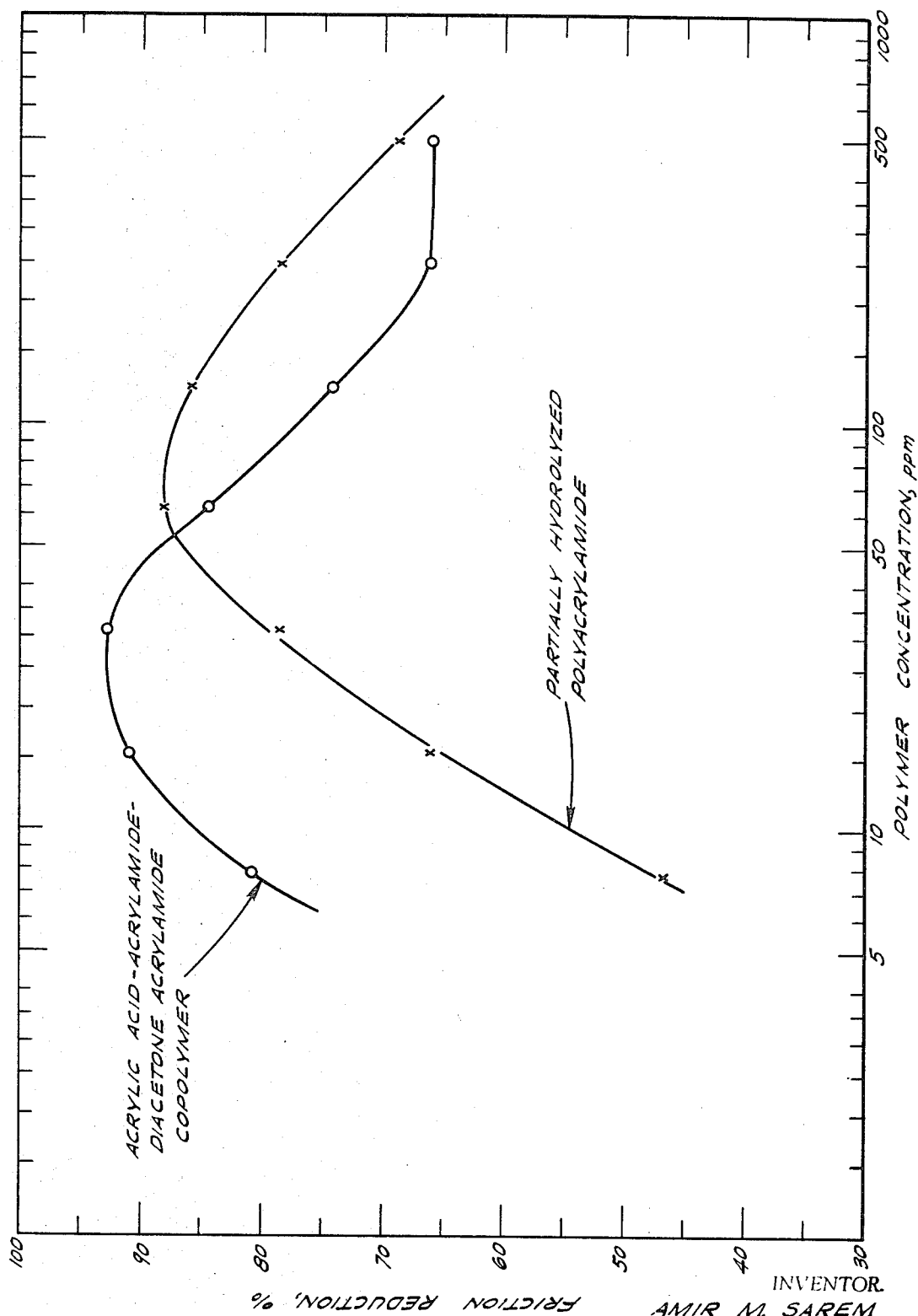
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ABSTRACT: A method for decreasing friction loss in the flow of an aqueous liquid through a conduit in which a small amount of acrylic acid-acrylamide-diacetone acrylamide terpolymer is added to the liquid. The method of this invention is particularly adapted to reducing friction loss in the flow of an aqueous fracturing fluid through a well and into a subterranean formation in a hydraulic fracturing process.



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METHOD OF DECREASING FRICTION LOSS IN A WELL FRACTURING PROCESS

This invention relates to the reduction of friction in flowing aqueous systems, and more particularly to a method of hydraulically fracturing subterranean earth formations whereby the pressure drop or friction loss due to the passage of the fracturing fluid through the well is decreased.

It is well known that in the movement of fluids, friction is encountered and thus energy must be expended to overcome the resistance to flow. This energy loss is generally apparent from the pressure drop obtained in moving the fluids a given distance through a conduit, and is approximately proportional to the square of the velocity of the fluid. Thus, in an operation where a high velocity is required, such as in the hydraulic fracturing of oil and gas wells, extremely high pressure drops are encountered, resulting in the loss of a large amount of energy to pump or move the fluid. In fracturing earth formations penetrated by a well, it is essential to inject a sufficient amount of fracturing fluid to build up the required pressure in the well sufficiently to produce cracks or fractures in the earth formation. Pressures as high as 3,000 to 10,000 pounds per square inch measured at the surface are often required to effect the required fracturing. Certain seepage of the fluids being pumped into the well is obtained so that it is necessary to inject the fluid into the well at high velocities to obtain the required pressure buildup. Even though fluid loss additives are added to the fracturing fluids to limit seepage, the fluid loss and the penetration of the fluid into the formation along the newly established fracture planes is sufficiently large as to require high fracturing fluid injection rates which result in high fluid velocities. In the attempt to increase these injection rates, efforts have been concentrated in increasing the capacity of pumping equipment. As a result, greatly increased hydraulic horsepower has been available to achieve increased injection rates and fluid pressures. However, the extent to which fracturing pressures and injection rates can be increased is not only limited by economic considerations due to higher pumping costs; but also because casing, tubing and well head maximum pressure ratings cannot be exceeded. Also, the effective pressure at the fracturing zone is further limited at higher injection rates as an increasing proportion of the developed pressure is consumed in friction loss, the effective fracturing pressure being the sum of the well head pressure and the static head at the fracture zone, less the friction loss through the flow conduits. Thus, a method whereby the friction loss due to the injection of fluid in the well can be decreased is highly desirable.

Accordingly, it is an object of this invention to provide a method of reducing the friction loss of an aqueous liquid flowing through a conduit. It is a further object of this invention to provide a method of fracturing wells whereby the pressure drop due to flow within the conduit is materially decreased. Another object of this invention is to provide a method of fracturing wells whereby the fracturing process can be completed at reduced surface pressure. Other objects and advantages of the invention will be apparent to those skilled in the art from the description thereof which follows.

Briefly, this invention contemplates reducing the friction loss in the flow of an aqueous liquid through a conduit by adding a small amount of acrylic acid-acrylamide-diacetone acrylamide terpolymer to the aqueous liquid. The polymer is dissolved in the aqueous liquid to provide therein a low concentration of the polymer. The dissolved polymer, in rather dilute concentration, imparts increased viscosity to the liquid to beneficially affect the solids-carrying property of the fluid. Additionally, there is imparted to the fluid the property of reduced flow resistance, or drag, as the fluid flows through a closed conduit. In one specific embodiment of the invention, the aqueous polymer solution has suspended therein finely divided, water-insoluble solid particles which function as fluid loss additives to reduce the quantity of fluid entering the formation due to natural permeability and previously existing crevices, fractures, and flow channels therein. Larger size, water-insoluble, oil-soluble particles serving as selective

plugging agents and propping agent spacers, as will be more fully described, and conventional nonsoluble solid propping agents can also be suspended in the aqueous polymer fracturing fluid.

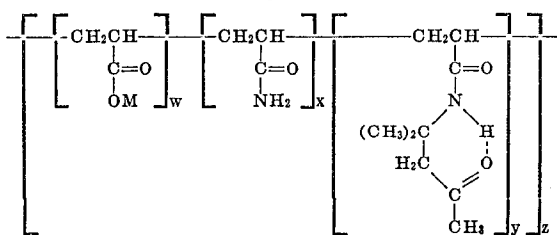
The FIG. graphically illustrates the comparative friction reducing abilities of aqueous solutions of acrylic acid-acrylamide-diacetone acrylamide terpolymer of the present invention and of partially hydrolyzed polyacrylamide, respectively, as a function of polymer concentration.

The high molecular weight acrylic acid-acrylamide-diacetone acrylamide terpolymer employed as the viscosity modifying agent exhibits the unusual property of increasing the viscosity of water within which it is dissolved, while simultaneously effecting decreased resistance to flow. From a theoretical standpoint, the decrease in flow resistance of the terpolymer solution is believed attributable to the flow modifying effect of the dissolved polymer, wherein the flow pattern of the fluid somewhat resembles that obtained under conditions of laminar flow. According to the well-known flow concept, so long as the critical Reynolds Number of a fluid medium flowing through an enclosed conduit is not exceeded, the fluid moves generally axially along the conduit in laminae. Above the critical Reynolds Number, secondary irregularities, or turbulence, are imposed on the flow pattern with a resultant increase in eddies caused by molecular collisions in the broken laminae. This phenomenon represents the change from laminar, through transition, to turbulent flow patterns. Moreover, the onset of turbulence is accelerated by any irregularity or entrance condition which will distort the flow pattern. As turbulence increases, energy loss due to random motions and to molecular collisions becomes much greater, resulting in greater friction loss.

The acrylic acid-acrylamide-diacetone acrylamide terpolymer macromolecule, because of dissimilarity of the side chain structure, tends to remain in a straight, or uncoiled, chain structure in aqueous solution. Under shear stress, such as results from fluid flow through a closed conduit, it is believed that the long chain terpolymer molecules are aligned substantially axially with the direction of fluid flow. Further, the side chains of these molecules become interlocked with those of adjacent molecules, forming elastic flexible dividers which separate the water molecules into enclosed compartments moving along the flow conduit. Nearly all of the molecular components of the fluid are retained within their own laminae with the polymer structure serving as flow guides. Moreover, the dividers dampen any turbulence that is imposed upon the flow pattern by irregularity or entrance condition. Thus, the dissolved polymers reduce energy loss due to random motions and to molecular collisions, and make more energy available for sustaining a high fluid flow rate.

However, without regard to the foregoing theoretical consideration, and for these or as yet unexplained reasons, high molecular weight acrylic acid-acrylamide-diacetone acrylamide terpolymers impart an increase in viscosity to an aqueous fracturing fluid and simultaneously effect a substantial reduction in the resistance to flow when the aqueous polymer solution is passed through a closed conduit under turbulent flow conditions. Thus, the present invention embodies a method of improving the hydraulic fracturing of earth formations through the use of aqueous compositions rendered more viscous, yet less resistant to flow, by the incorporation therein of acrylic acid-acrylamide-diacetone acrylamide terpolymers prepared by the copolymerization of the monomers in aqueous solution in the presence of organoboron catalyst. It is among the advantages of the invention that this terpolymer is adsorbed in underground strata to only a minimal extent. It is a further advantage of the invention that said terpolymers are not rendered insoluble by the presence in the solution of concentrations of calcium ions and sodium ions such as are commonly encountered in oil field brines. Yet another advantage of the invention resides in the fact that only very small amounts of the polymer are required to achieve the beneficial effects.

The polymeric agents found useful in decreasing the friction loss in flowing aqueous systems are substantially linear, water-soluble polymers having amide, carboxyl and diacetone substituted amide groups arranged along a substantially carbon-carbon chain. The term "acrylic acid-acrylamide-diacetone acrylamide terpolymer", as employed herein, is inclusive of the hydrolyzed polymer wherein the carboxyl groups are in the acid form and also of such polymers wherein the carboxyl groups are in the salt form. Thus, for example, the terpolymer may exist in the hydrolyzed form wherein the carboxyl groups are hydrolyzed to acids, or wherein the carboxyl groups are in the form of salts of ammonium, alkali metal, alkaline earth metal and the like. Although the length of the molecular chain and the proportion and distribution of amide, carboxyl and diacetone substituted amide groups are variable, the terpolymers useful in the practice of this invention are characterized by the generalized formula



wherein M is a cation and can be hydrogen, ammonium, alkali metal, alkaline earth metal, or other metal that will replace hydrogen to form a carboxylate salt; and wherein w , x and y represent respectively the average number of acrylic acid monomer units, acrylamide monomer units and diacetone acrylamide monomer units in the polymer per 100 monomer units of the polymer. The molar proportion of acrylic acid monomer in the polymer is thus represented by the fraction $\frac{w}{100}$ the proportion of acrylamide by the fraction $\frac{x}{100}$ and the proportion of diacetone acrylamide by the fraction $\frac{y}{100}$ and the sum of w , x and y equals 100. The subscript z represents the average number of 100 monomer units in the polymer. The diacetone acrylamide group has been shown in the form of a ring structure. However, the bonding or association between the hydrogen and the keto oxygen is relatively weak, and it is to be understood that the diacetone group may be in the form of a linear chain.

The proportions of the various monomer units in the polymer, their distribution along the carbon-carbon chain, and the length of the chain can vary over a wide range, thereby providing a family of polymers having different molecular weights and water solubilities, and differing in other important properties. Thus, while the composition and structure of the polymers of this invention can vary over wide ranges, it has nevertheless been found that a number of useful acrylic acid-acrylamide-diacetone acrylamide copolymers can be defined by the foregoing generalized formula wherein w is from about 10—50, x is from about 25—85, y is from about 1—25, and z varies up to about 8,000.

A material that possesses superior properties as a friction reducing agent for water is an acrylic acid-acrylamide-diacetone acrylamide terpolymer according to the foregoing generalized formula wherein w is from about 15—35, x is from about 45—80, and y is from about 2—15. Further, to prevent a loss in water solubility, the cation ion M is preferably a monovalent cation such as hydrogen, ammonium, or an alkali metal such as sodium, potassium, lithium, rubidium and cesium.

The terpolymers in accordance with the present invention that are particularly useful as friction reducing additives are characterized by high molecular weight and the ability to increase the viscosity of aqueous solutions of the polymer. The terpolymers found useful as friction reducing agents are characterized by average molecular weights of at least

500,000 and molecular weights of 1,000,000 or more are preferred, with some of the more preferred polymers having molecular weights up to 40,000,000 or more. The molecular weight of the terpolymer is correlated with the viscosity of a standard solution of the polymer under controlled conditions. Accordingly, it has been found that the terpolymers preferred for use as friction reducing additives are those characterized by a viscosity of at least 3 centipoises for a 0.05 percent by weight solution thereof in an aqueous 3 percent by weight sodium chloride solution at a temperature of 25°C. as determined by a Brookfield viscosimeter equipped with a UL adapter spindle and operated at a speed of 30 r.p.m.

The acrylic acid-acrylamide-diacetone acrylamide terpolymers in accordance with this invention are prepared by copolymerizing acrylic acid, acrylamide and diacetone acrylamide in aqueous solution with an organoboron catalyst. Diacetone acrylamide, also known as (N-acrylamide), is a water-soluble substituted acrylamide that can be prepared by the reaction of acrylamide and diacetone alcohol in the following manner: $\text{CH}_2\text{CHCONH}_2 + \text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH} \rightarrow \text{CH}_2\text{CHCONHC}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3 + \text{H}_2\text{O}$. An aqueous solution of the monomers is prepared and polymerization initiated by the addition of organoboron catalyst. The resulting polymeric product is a viscous liquid or a gel comprising a substantially linear water-soluble copolymer having a minimum of cross linking and which possesses superior properties, these properties being to some extent controlled by the selection of monomer proportions and the reaction conditions.

The polymerization catalysts useful in the practice of this invention are organoboron compounds, and particularly organoboron compounds having the following generalized formula



wherein R_1 , R_2 and R_3 are alkyl radicals, and preferably are alkyl radicals having less than about four carbon atoms in the alkyl group. Thus, the preferred catalysts of this invention comprise a group of trialkylboron compounds having methyl, ethyl, propyl, butyl and iso-butyl substituent groups. These compounds can be mixed alkylborons in that two or more different alkyl groups are contained in the molecule, or the alkyl groups can be the same. Exemplary of this latter class of compounds are trimethylboron, triethylboron, tripropylboron, tri(n-butyl)boron and tri(isobutyl)boron. Further, it is within the scope of this invention to employ a mixture of the foregoing trialkylboron compounds as the catalytic polymerization agent. Also, various boronous anhydrides and boronites exhibit the requisite catalytic properties and can be used to prepare the terpolymer compositions of this invention.

While the exact mechanism of the polymerization reaction of this invention is not clearly understood, it is believed that the reaction is of the free radical type initiated by a peroxide formed by the reaction of organoboron with trace quantities of oxygen. The organoboron is also believed to complex with the free radical at the end of the polymer chain in such a way that termination of the reaction becomes less likely, resulting in the formation of polymers having molecular weights higher than would be produced in the absence of the organoboron compound. Further, the organoboron catalyzed reaction may result in a polymer having a different composition or a different distribution of substituent groups along the polymer chain than would be obtained by other methods of polymerization. Thus, while I do not desire to be held to any particular theory of operation, it has nevertheless been demonstrated that polymer compositions prepared by the method of this invention are superior in many important properties to those prepared by the heretofore known technique.

Although the presence of trace quantities of oxygen are believed necessary to initiate the free radical polymerization reaction, the presence of excess oxygen terminates the polymerization reaction prematurely, thus resulting in a lower molecular weight polymer product. While, in a preferred em-

bodiment of this invention, it is desirable that excess oxygen be removed prior to initiating the reaction, polymerization with organoborons may be successful even though a relatively large quantity of oxygen is initially present in the reaction mixture since most of the oxygen is consumed by reaction with the organoboron to produce more highly oxidized boron compounds which are not effective in providing free radicals. Thus, it is within the scope of this invention to control the amount of oxygen in contact with the reactant solution during the polymerization reaction. Oxygen can be controlled to suitable levels by evacuating and purging the reaction vessel of air prior to initiating the polymerization reaction to remove the excess undissolved oxygen from the system, the optimum content of oxygen dissolved in the reactant solution being a molar concentration about equal to the molar concentration of the organoboron compound present. Thus, it is preferred in most applications that the reactant monomer solution contain between about 15 and about 600 p.p.m. of dissolved oxygen based on the monomer content of the solution. Excess dissolved oxygen can be removed from the reactant solution, if desired. Conversely, in those cases where the reaction mixture is totally devoid of the necessary quantity of oxygen to initiate the free radical reaction, it is within the scope of this invention to add oxygen to the reaction mixture.

The polymerization of the acrylic monomers usually can be initiated at room temperature although some mild heating may be necessary in certain polymerization reactions. These reactions are exothermic and are accompanied by a release of heat causing an increase in reactant temperature. While normal temperature increases can be accommodated with no particular problem, too high of a rate for the exothermic polymerization reaction would cause a significant increase in temperature, especially after the solution has thickened so that heat dissipation is impaired. With increased temperature, further increases in polymerization rate result. This tendency toward "runaway" polymerization is greater with a higher concentration of monomers in solution. Higher temperatures can also cause cross linking of the polymer resulting in polymers of reduced water solubilities and other inferior properties. With most reactant systems it is preferred that the reaction temperature be controlled below about 65°C. Accordingly, it is within the scope of this invention to control the concentration of monomers below the level resulting in excessive temperature increases resulting in "runaway" polymerization, and more particularly at temperatures below about 65°C. In most applications, excessive temperatures are not encountered at reactant concentrations below about 30 weight percent monomer mixture. Further, it is within the scope of the invention to cool the reaction mixture sufficiently to prevent excessive temperatures. Although the minimum amount of the organoboron catalyst required to initiate the reaction will depend somewhat on the oxygen content of the system, as hereinafore disclosed, it has nevertheless been found that polymerization of most systems can be initiated at catalyst concentrations of 5—200 p.p.m. of boron based on the weight of monomers present. Since the molecular weights of the various catalysts are different, catalyst additions are conveniently based on boron content, it being understood that different amounts of the various organoboron compounds must be employed to provide equivalent quantities of boron.

The organoboron catalysts useful in the practice of this invention are for the most part oleaginous materials having limited solubility in water. This property of the catalyst limits its effectiveness as undissolved droplets of the organoboron compound accumulate in the aqueous reactant solution and do not readily contribute to the polymerization. More efficient dispersion of the catalyst can be achieved by first dissolving the catalyst in a mutual solvent which is miscible with water, at least in the range of concentrations encountered. Suitable solvents for the organoboron catalysts, and in particular for the preferred trialkylboron catalysts, which are also miscible with water include dioxane, dimethylsulfoxide, and low molecular weight alcohols and ketones. The catalyst is dissolved in a con-

venient volume of solvent and this solution added to the reactant monomer solution to initiate the polymerization reaction. Although the concentration of the catalyst in the solution is not critical, this solution can conveniently contain from about 5 to about 50 parts of an organoboron compound, such as trialkylboron, per part of solvent.

Also, certain of the trialkylborons are sufficiently volatile that they can be added to the reactant monomer solution in vapor form. Thus, particularly in the case of those trialkylborons containing primarily methyl and ethyl substituent groups, the catalyst can be vaporized and contacted with the monomer solution by bubbling the catalyst vapor into the reactant solution. Alternatively, catalyst vapor can be admixed with an inert carrier gas, such as helium or nitrogen, and bubbled into the monomer solution. With this mode of catalyst addition it may be advantageous to recycle the inert gas to avoid the loss of catalyst in the gas exiting the solution.

In carrying out the invention, the terpolymer is dissolved in water in any suitable fashion to provide a solution having the desired viscosity and flow properties. Alternatively, the terpolymer can be dissolved in brine or an aqueous solution of the polymer can be diluted with brine to form a solution having ionic constituents similar or identical to those in the connate water in the oil field where the fracturing operation is to be performed. In general, with the high molecular weight acrylic acid-acrylamide-diacetone acrylamide terpolymers preferably employed, that is with polymers having a molecular weight of at least 500,000, it is desirable to employ less than about 500 p.p.m. by weight of the polymer in the fracturing fluid. In many applications, it is preferred that the polymer be added to the aqueous liquid to establish therein a concentration of about 10—100 p.p.m. of the polymer. An even more preferred treatment useful in many applications is to add the aforementioned polymer to the aqueous solution in an amount sufficient to establish therein a concentration of 10—50 p.p.m. In practice, the fracturing fluid can have a viscosity of from slightly over that of pure water (1.0 centipoise at 20°C.) to about 1000 centipoises. The exact polymer addition to be employed for maximum efficiency will depend on the size of the flow conduits, the formation depth, the nature of the formation, injection rates, temperature and the nature of other additives or constituents added to the fracturing fluid.

As previously mentioned, various water-insoluble, finely divided solid fluid loss additives, such as silica flour, clay and commercially compounded solid materials for example, can be dispersed in the viscous fracturing fluid so as to partially or completely plug the formation face about the periphery of the well bore and along the fracture plane, and thereby reduce the loss of fracturing fluid to the formation. Although these materials are generally satisfactory from the standpoint of reducing fluid loss and increasing fracture efficiency, their use frequently causes irreparable damage to the formation as permanent plugs are formed resulting in reduced oil permeability. Although some of the deposited material can be removed from the exposed formation about the periphery of the well bore by well known techniques, the material penetrating into the formation, particularly along the fracture planes, is extremely difficult to remove. Formation damage can be materially decreased by the use of an oil-soluble fluid loss additive which is dissolved by the connate oil, thus eliminating the problem of permeability loss because of permanent plugging. Although any of the aforementioned oil-insoluble fluid loss additives can be employed with the viscous fracturing fluid of this invention, permanent formation damage is likely to result from the deposition of insoluble particles in the formation, as with conventional fracturing fluids. For this reason, oil-soluble fluid loss additives are preferred.

Any oil-soluble, relatively water-insoluble, finely divided solid particulate matter which can be suspended or dispersed in the viscous fracturing fluid can form a suitable fluid loss additive. Such materials include naphthalene and other oil-soluble, water-insoluble, normally solid hydrocarbons, and the like. Preferred oil-soluble, water-insoluble fluid loss additives

can be prepared from homogeneous solid solutions of hydrocarbon wax such as paraffin wax, of a single or multiple melting point grade, melting above about 120°F., and polymers including (1) addition polymers of an olefin having between two and four carbon atoms in the monomer molecules; (2) copolymers of an olefin having between two and four carbon atoms and an alkyl acrylate containing not more than four carbon atoms in the alkyl group, such as esters formed by the reaction of acrylic acid and an alcohol having no more than four carbon atoms; (3) copolymers of an olefin having between two and four carbon atoms and esters formed by the reaction of butenic acid and an alcohol having no more than four carbon atoms; and (4) copolymers of an olefin having between two and four carbon atoms and as ester formed by the reaction of acetic acid and an unsaturated alcohol having no more than four carbon atoms. Desired properties of strength, ductility, solubility, melting point, and density not obtainable with either hydrocarbon wax or polymer alone can be achieved by homogeneous solid solutions of the two. Preferred polymer component materials include polyethylene, polypropylene, polybutylene, copolymers of ethylene and vinyl acetate, and copolymers of ethylene and ethyl acrylate. These polymer component materials can be homopolymers of polymerizable monomers selected from the above-disclosed compounds, or two or more of these monomers can be copolymerized to yield a polymeric component material having improved properties not obtainable with the homopolymers. Compositions having even further improved properties can be prepared by blending two or more of these polymer component materials with wax to form the aforementioned homogeneous solid solutions.

When used as fluid loss additives in the viscous fracturing fluid of this invention, it is preferred that the water-insoluble solid particles be extremely finely divided so as to effectively enter into small pores and flow channels in the formation. Most preferably these particles are of a size which will pass a number 20 U.S. Standard sieve.

Also, the foregoing water-insoluble, oil-soluble wax-polymer compositions are highly effective as plugging agents adapted for use in hydraulic fracturing, the particles functioning as temporary plugging agents in oil-carrying fractures and as permanent plugging agents in water-carrying fractures. By means of a stepwise fracturing and plugging technique, multiple oil-carrying fractures not otherwise obtainable can be formed in the oil-bearing formation without causing water influx.

Additionally oil-soluble solid particles of the foregoing composition can be effectively employed as propping agent spacers, in which case a mixture of these particles and permanent propping agent is suspended in the fracturing fluid and injected through the well and into the fracture. The mixed particles are randomly deposited in the fracture. On contact with connate oil, the oil-soluble particles are dissolved leaving the remaining permanent propping agent in spaced relationship and thereby attaining increased permeability along the fracture plane. For application as either plugging agents or as propping agent spacers, oil-soluble, water-insoluble solid particles of the above wax-polymer composition within the size range passing a number 4 and being retained on a number 20 U.S. Standard sieve are preferred. Where the oil-soluble particles function only as propping agent spacers, it is preferred that they be of the same size range as the propping agent with which they are employed.

A particularly preferred wax-polymer composition for use in fluid loss control, temporary plugging of oil-carrying fractures, and for propping agent spacer applications is a homogeneous solid solution of refined paraffin wax melting between about 130°F. and about 165°F. and not more than

about 40 percent by weight copolymer ethylene and ethyl acrylate or vinyl acetate. Addition of small quantities of surfactant to the fracturing fluid improves the water wetting property of the solid particles and facilitates their suspension in the viscous fracturing fluid.

Other preferred particulate solid solutions include various blends of the aforementioned water-insoluble polymers and halogenated aromatic hydrocarbons or alcohols melting above about 120°F., which blends can also contain wax, and blends of these polymers with wax and resin.

These homogeneous solid solutions of waxes and polymers are blended products readily prepared by melting the individual components and then combining the resulting liquids in the proper proportions. Alternatively, the solid ingredients can be combined in the proper proportion and then melted to achieve a homogeneous liquid solution. In either case, the proportion of each component is selected to impart the previously disclosed important properties to the final solidified product.

As previously disclosed, the composition must be formed into solid particles to be advantageously employed in the fracturing process described herein, and most preferably is formed into small spherical particles of a size range selected for the particular treating application. The molten compositions of this invention are readily formable into solid particles of the desired size by several techniques, such as prilling, dispersion, extrusion, etc., and the solid composition can be formed into particles by grinding, cutting, tearing, etc. One technique of manufacture wherein solid particles of the composition are formed from molten material comprises violently agitating the molten composition within a body of nonsolvent liquid, such as water, containing a finely divided solid, such as calcium carbonate. The subdivided molten material, maintained in constant movement while cooling below the solidification point of the composition, usually assumes a somewhat spherical particle shape. Cooling or quenching of the subdivided particles can be carried out in any convenient manner, but usually comprises the introduction of large amounts of additional cool, nonsolvent liquid to the subdivided particles dispersed in the original body of nonsolvent liquid. Alternatively, ice can be added to the nonsolvent liquid as coolant.

The invention can be illustrated further by the following examples which are illustrative of specific modes of practicing the invention and are not intended as limiting the scope of the invention as defined in the appended claims.

EXAMPLE I

The comparative friction reducing abilities of acrylic acid-acrylamide-diacetone acrylamide and partially hydrolyzed polyacrylamide are determined with a Halliburton Friction Reduction Meter. This apparatus comprises means for pumping a liquid through a section of conduit at constant flow rate and for measuring the pressure drop through the conduit.

Base conditions are established by determining the friction loss of water. A series of tests is then made using aqueous solutions of a commercial partially hydrolyzed polyacrylamide containing various concentrations of the polymer. The percentage reduction in friction loss is determined as the difference in the friction loss with water and with polymer solution expressed as a percentage of the friction loss with water.

The above tests are repeated using an aqueous solution of acrylic acid-acrylamide-diacetone acrylamide terpolymer prepared by copolymerizing an aqueous 15 weight percent solution of a monomer mixture comprising 27 weight percent acrylic acid, 63 weight percent acrylamide and 10 weight percent diacetone acrylamide in the presence of triethylboron catalyst and neutralizing the resulting polymer to a pH of about 9.

The results of these tests are shown in the following table:

Polymer	Friction loss reduction, percent						
	Polymer concentration, p.p.m.						
	500	250	125	62.5	31.3	15.6	7.8
Run:							
1..... Polyacrylamide ¹	68.5	78.2	85.9	87.9	78.2	65.9	46.5
2..... AADA copolymer ²	65.9	65.9	74.0	84.2	92.8	90.9	80.7

¹ Partially hydrolyzed polyacrylamide marketed by the Dow Chemical Company under trade name Pusher 500.

² Acrylic acid-acrylamide-diacetone acrylamide terpolymer.

These data are graphically represented in the attached drawing. It is apparent that the acrylic acid-acrylamide-diacetone acrylamide terpolymer effects a greater reduction in friction loss than does partially hydrolyzed polyacrylamide, and is effective at lower concentrations than the polyacrylamide.

EXAMPLE 2

A subterranean oil-bearing formation penetrated by a well is fractured in accordance with the method of this invention. The well is cased to a depth below the producing zone with 7-inch steel casing, which is perforated with four $\frac{3}{8}$ -inch perforations per foot between the interval of 6873 feet and 6880 feet. Tubing is set to a depth of 6870 feet and a packer installed just above the terminus of the tubing.

A fracturing fluid is prepared by dissolving acrylic acid-acrylamide-diacetone acrylamide terpolymer and a bacteria control additive in available fresh water. The polymer is added in an amount equivalent to 30 p.p.m. and the bacteria control additive at 0.9 gallons per thousand gallons of fluid. The bacteria control additive contains a surface active agent which facilitates dispersion of the particulate additives suspended in the fluid.

The fracturing fluid is injected into the well at injection rates of 18 to 20 barrels per minute at a well head pressure of between 2500 and 2600 p.s.i.g. Solid particles of various fluid loss additives, temporary plugging agents, propping agents and propping agent spacers can be suspended in the fracturing fluid in conventional manner.

Various embodiments and modifications of this invention have been described in the foregoing description and examples, and further modifications will be apparent to those skilled in the art. Such modifications are included within the scope of this invention as defined by the following claims.

I claim:

1. A method for reducing the friction loss resulting from the flow of an aqueous liquid through a conduit, which comprises flowing said liquid containing a small amount of a water-soluble acrylic acid-acrylamide-diacetone acrylamide terpolymer through said conduit, said terpolymer being formed by the copolymerization of acrylic acid, acrylamide and diacetone acrylamide in aqueous solution in the presence of an organoboron catalyst.

2. The method defined in claim 1 wherein said aqueous liquid contains less than about 500 p.p.m. of said terpolymer.

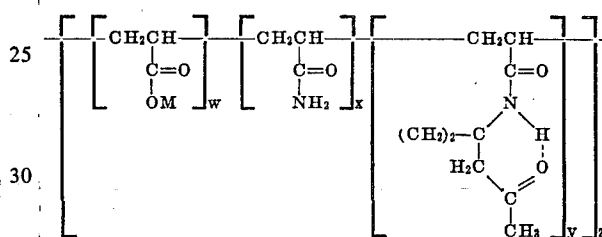
3. The method defined in claim 1 wherein said aqueous liquid contains between about 10—100 p.p.m. of said terpolymer.

4. The method defined in claim 1 wherein said aqueous liquid contains between about 10—50 p.p.m. of said terpolymer.

5. In the process of hydraulically fracturing an earth formation penetrated by a well wherein an aqueous fracturing fluid is injected through the well and into the formation, the improvement of decreasing the friction loss resulting from the

flow of the aqueous fracturing fluid which comprises injecting said fracturing fluid having added thereto a small amount of a water-soluble acrylic acid-acrylamide-diacetone acrylamide terpolymer prepared by the copolymerization of acrylic acid, acrylamide and diacetone acrylamide in aqueous solution in the presence of organoboron catalyst.

6. The method defined in claim 5 wherein said acrylic acid-acrylamide-diacetone acrylamide terpolymer is characterized by the following generalized formula



wherein M is a cation; w, x and y represent respectively the average number of acrylic acid monomer units, acrylamide monomer units and diacetone acrylamide monomer units in the polymer per 100 monomer units of the polymer, the sum of w, x and y totaling 100; and z represents the average number of 100 monomer units in the polymer.

7. The method defined in claim 6 wherein w is from about 10—50, x is from about 25—85, y is from about 1—25, and z varies up to about 8000.

8. The method defined in claim 6 wherein M is a monovalent cation selected from the group consisting of hydrogen, ammonium and alkali metals; w is from about 15—35, x is from about 45—80, y is from about 2—15, and z varies up to about 8000.

9. The method defined in claim 5 wherein said acrylic acid-acrylamide-diacetone acrylamide terpolymer is further characterized by a viscosity of at least about 3 centipoises for a 0.05 percent by weight solution thereof in an aqueous 3 percent by weight sodium chloride solution at 25°C. as determined with a Brookfield viscosimeter equipped with a UL adapter spindle and operated at 30 r.p.m.

10. The method defined in claim 5 wherein said polymer is added to the fracturing liquid in an amount sufficient to establish therein a concentration of less than 500 p.p.m. of said polymer.

11. The method defined in claim 5 wherein said polymer is added to the fracturing fluid in an amount sufficient to establish therein a concentration of 10—100 p.p.m.

12. The method defined in claim 5 wherein said polymer is added to the fracturing fluid in an amount sufficient to establish therein a concentration of 10—50 p.p.m.

13. The method defined in claim 5 in which discrete particles of a solid material are suspended in said fracturing fluid.

14. The method defined in claim 5 in which discrete solid particles of a water-insoluble, oil-soluble homogeneous solid solution of wax and polymer are suspended in said fracturing liquid.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,537,525 Dated November 3, 1970

Inventor(s) Amir M. Sarem

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 5, column 10, line 16 "acpylic" should be -- acrylic

Claim 6, line 28, "(CH₂)" should be -- (CH₃) --.

Claim 7, line 40, "if" should be -- is --.

SIGNED AND
SEALED
FEB 9 1971

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents