

[54] **FRICTION REDUCING IN FLOWING HYDROCARBON FLUIDS**

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[51] **Int. Cl.** .....C10m 7/26, E21b 43/26, F17d 1/16

[58] **Field of Search** .....166/308; 137/13; 252/8.55 R, 252/8.5 C, 8.5 E, 56 R; 260/29.6 R, 33.4 R, 33.6 R, 29.6 ME

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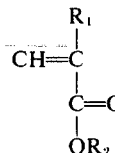
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[57] **ABSTRACT**

This disclosure is directed to a method and composition useful in reducing the friction loss in flowing hydrocarbon fluids. The composition is an emulsion consisting essentially of a homopolymer or copolymer of



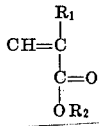
where "R<sub>1</sub>" is H or CH<sub>3</sub> and "R<sub>2</sub>" is an alkyl group of 8 to 18 carbon atoms, a glycol and water. The method comprises mixing the emulsion with the hydrocarbon fluid and then adding a lower alkyl alcohol which causes the polymer to be transferred from the emulsion phase to a hydrocarbon solution.

**12 Claims, No Drawings**

## FRICITION REDUCING IN FLOWING HYDROCARBON FLUIDS

### BACKGROUND OF THE INVENTION

This invention relates to reducing friction loss in flowing hydrocarbon fluids. More particularly, it relates to a method for reducing the friction loss of hydrocarbon fluids flowing in a conduit by adding to the hydrocarbon fluid a friction reducing additive comprising an emulsion of a polymer of



where "R<sub>1</sub>" is H or CH<sub>3</sub> and "R<sub>2</sub>" is an alkyl group of eight to 18 carbon atoms, a glycol and water.

In the process of transferring liquids in conduits, the problem of high friction loss caused by nonlaminar flow is often encountered. This frictional loss is especially great when the fluid is pumped under high pressures and at high velocities. In order to compensate for this friction loss, a considerable amount of energy must be expended in moving the fluids.

The two most common industrial operations in which friction loss is a major problem are oil well fracturing and the transmission of oil for considerable distances in petroleum pipelines. It is obvious that a reduction in friction loss would permit lower surface operating pressures, reduced power requirements and greater pressure at the bottom of the well bore in a fracturing operation and also increased flow rates and reduced power requirements in the transmission process. Thus, it can readily be seen that the reduction of friction in flowing hydrocarbons fluids is greatly desired.

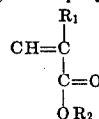
In the past, various materials have been proposed and used as friction reducers in hydrocarbon fluids. For example, see U.S. Pat. No. 3,288,577 which discloses the use of certain high molecular weight polymers as friction reducers. See also U.S. Pat. No. 3,351,079 which discloses the use of ethylene propylene copolymers and U.S. Pat. No. 3,215,154 which discloses the use of polyisobutylene. Finally, see U.S. Pat. No. 3,493,000 which discloses the use of polydimethylsiloxane as a friction reducer in hydrocarbon fluids.

Recently, it has been found that certain polyacrylates and methacrylates are excellent friction reducers in hydrocarbon fluids. However, the solubility rate of these polymers in crude oil is slow and in order to use the polymer readily, it must be predissolved in oil, kerosene or the like. In addition, the polymers are usually prepared as aqueous emulsions and it has heretofore been necessary to recover the polymers from the emulsions before adding them to the oil or kerosene. These additional steps of recovering the polymer and dissolving it increase the cost of using the polymer. It would therefore be desirable to be able to use the polyacrylate and polymethacrylate emulsions directly without having to recover them and then dissolve them. However, the aqueous emulsions of the polymers do not have temperature stability at the low temperatures which are often encountered in the oil field processes especially those temperatures encountered in the winter months in Alaska and other areas. Therefore, even if the emulsion can be used directly, it is desirable that it have temperature stability.

### SUMMARY OF THE INVENTION

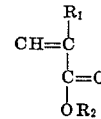
We have found a method of utilizing an emulsion of a polyacrylate or polymethacrylate to reduce friction in flowing hydrocarbons without having to isolate the polymer from the emulsion. In addition, we have found an emulsion which has good temperature stability.

The emulsion of our invention comprises (a) from 20 to about 60 percent by weight of a polymer of



where "R<sub>1</sub>" is H

or CH<sub>3</sub> and "R<sub>2</sub>" is an alkyl group of eight to 18 carbon atoms, (b) from 10 to 50 percent by weight glycol, (c) from 10 to 60 percent by weight water, and (d) from 1 to 10 percent by weight emulsifying agent (surfactant). The preferred emulsion of our invention comprises (a) from 25 to 50 percent by weight of a polymer of



where "R<sub>1</sub>" is H or CH<sub>3</sub>

and "R<sub>2</sub>" is an alkyl group of eight to 18 carbon atoms, (b) from 15 to 40 percent by weight glycol, (c) from 20 to 50 percent by weight water, and (d) from 1 to 5 percent by weight emulsifying agent.

The useful glycols of our invention include ethylene glycol, propylene glycol, diethylene glycol and the like. The preferred glycol is ethylene glycol.

The polymer may be a homopolymer of the acrylate or methacrylate or it may be a copolymer of the acrylate or methacrylate and up to 10 percent by weight of one or more suitable comonomers. Some of the suitable comonomers are the lower alkyl acrylates and methacrylates such as methylmethacrylate, ethyl acrylate, butyl acrylate and the like. Other suitable comonomers include the dialkyl diallyl ammonium chlorides such as dimethyl diallyl ammonium chloride, acrylamide and the N-substituted acrylamides such as diacetone acrylamide. The comonomer is used to impart various desirable properties to the final polymer. For example, the use of dimethyl diallyl ammonium chloride as the comonomer imparts a slight cationic charge to the final polymer and the use of acrylamides provide sites for hydrogen bonding, either of which gives the polymer a hydrophilic property. This property is desirable since the presence of hydrophilic sites on the polymer will enhance the performance of the polymer in hydrocarbon fluids containing small amounts of polar materials such as water, alcohols, thiols and the like.

The preferred polymer of our invention is polyisodecylmethacrylate. Therefore, when using the preferred polymer, the emulsion of our invention comprises (a) from 20 to about 60 percent by weight polyisodecylmethacrylate, (b) from 10 to 50 percent by weight glycol, (c) from 10 to 60 percent by weight water, and (d) from 1 to 10 percent by weight emulsifying agent (surfactant). Similarly, the preferred emulsion of our invention comprises (a) from 25 to 50 percent by weight polyisodecylmethacrylate, (b) from 15 to 40 percent by weight glycol, (c) from 20 to 50 percent by weight water, and (d) from 1 to 5 percent by weight emulsifying agent.

The emulsion of our invention may be prepared by polymerizing the acrylate or methacrylate monomer in an aqueous emulsion and then adding the glycol or the emulsion may be prepared by polymerizing the acrylate or methacrylate in a cosolvent system of the glycol and water. The use of the cosolvent system is the preferred method. The use of the cosolvent system lowers the raw material cost, increases the yield of polymer and, in general, facilitates the polymerization process. In addition, we have found that by emulsion polymerizing the monomer in the cosolvent system of water and glycol the resulting polymer gives better friction reduction than a polymer prepared via an aqueous emulsion.

As mentioned above, the polymer of our invention is prepared by an emulsion polymerization technique. In the emulsion polymerization, the water-insoluble monomer is emulsified in water/glycol cosolvent system by means of a surfactant. A polymerization initiator is added and the polymer is formed. The polymeric emulsion must then remain in a homogenous state. There must be no evidence of a phase separation even when subjected to freeze-thaw temperature cycles ranging from about -30° F. to about 90° F. The polymeric emulsions of our invention have these desired properties.

When polymerizing the acrylates and methacrylates of our invention in the cosolvent system or in plain water, it is possible to use either cationic, nonionic, anionic or amphoteric surfactants or a combination of different surfactants. We have made emulsions using all types of surfactants. However, we have found that anionic surfactants such as dioctyl sodium sulfosuccinate give the most stable emulsions, which are nearly free from coagulum. We have also found that many different polymerization initiators may be used in preparing the emulsions of our invention. Examples of some of the useful initiators are ammonium persulfate, potassium persulfate, azobisisobutyronitrile, tertiary butyl peroxyvalate, tertiary butylperoxide, benzoyl peroxide and the like. The preferred initiator of our invention is potassium persulfate.

The following examples illustrate the preparation and composition of the emulsions of our invention.

#### EXAMPLE 1

Into a one liter, four-necked flask equipped with stirrer, thermometer, reflux condenser and gas inlet tube was charged 200.0 grams of isodecylmethacrylate, 162.0 grams of ethylene glycol and 162.0 grams of water. The reaction mixture was purged with nitrogen for one and one-half hours. Then 16.8 grams of TRITON GR-5 (dioctyl sodium sulfosuccinate) was added to the mixture. The temperature was increased to 60° C and 0.06 grams of potassium persulfate was added. The reaction mixture exothermed to 70° C over a period of twenty minutes. The reaction was then allowed to proceed for three hours at a temperature between 60° and 70° C. The emulsion was placed in an atmosphere controlled at -30° F for twenty-four hours. It was then allowed to stand at room temperature ( $\approx$  70° F) for twenty-four hours. This cycle was repeated three times. The emulsion remained as a liquid with no phase separation nor formation of coagulum. This emulsion gave 64 percent friction reduction in a hydrocarbon fluid as compared to polyisobutylene which gave about 36 percent.

#### EXAMPLE 2

Into a one liter, four-necked flask equipped with stirrer, thermometer, reflux condenser and gas inlet tube was charged 200.0 grams of tridecylmethacrylate, 162.0 grams of ethylene glycol and 162.0 grams of water. The reaction mixture was purged with nitrogen for one and one-half hours. Then 16.8 grams of TRITON GR-5 (dioctyl sodium sulfosuccinate) was added to the mixture. The temperature was increased to 60° C and 0.06 grams of potassium persulfate was added. The reaction mixture exothermed to 70° C over a period of twenty minutes. The reaction was then allowed to proceed for three hours at a temperature between 60° and 70° C. The emulsion was placed in an atmosphere controlled at -30° F for twenty-four hours. It was then allowed to stand at room temperature ( $\approx$  70° F) for twenty-four hours. This cycle was repeated three times. The emulsion remained as a liquid with no phase separation nor formation of coagulum. This emulsion showed friction reduction properties of the same order of magnitude as polyisobutylene when tested in a hydrocarbon fluid.

#### EXAMPLE 3

Into a 250 ml., four-necked flask equipped with a stirrer, thermometer, reflux condenser and gas inlet tube was charged 50 grams of isodecylmethacrylate, 100 grams of water, and 2.5 grams of surfactant (sodium lauryl sulfate). The reaction mixture was then purged for one hour with argon. The temperature was increased to 60° C and 0.015 grams of potassium persulfate was added. The reaction was then allowed to proceed for three hours at a temperature between 60° and 70° C. The reaction mixture was cooled to room temperature and ethylene glycol added so that the resulting mixture was 28.6 percent by weight ethylene glycol. The emulsion was then placed in a freezer at -5° C for sixteen hours. The emulsion remained as a liquid with no phase separation nor formation of coagulum. This emulsion gave 60 percent friction reduction.

#### EXAMPLE 4

Into a 250 ml. flask equipped with a stirrer, thermometer, reflux condenser and gas inlet tube was charged 40 grams isodecylmethacrylate, 22 grams ethylene glycol, 38 grams water and 2 grams sodium lauryl sulfate. The reaction mixture was then purged for one hour with argon and heated to 60° C. Then 0.012 grams potassium persulfate was added and the reaction allowed to proceed for three hours at a temperature between 60° and 70° C. The emulsion was then subject to a freeze-thaw cycle ranging from -20° C to room temperature. The emulsion was stable with no phase separation nor coagulum. This emulsion gave 59 percent friction reduction.

#### EXAMPLE 5

Into a 250 ml., four-necked flask equipped with a stirrer, thermometer, reflux condenser and gas inlet tube was charged 50 grams of isodecylmethacrylate, 33 grams of ethylene glycol, 30 grams water and 2.5 grams TRITON GR-5. The reaction mixture was purged for one hour with nitrogen and heated to 60° C. Then 0.015 grams of potassium persulfate was added and the reaction allowed to proceed for three hours at 60° to 70° C. The resulting emulsion was stable and had no coagulum. The emulsion gave a friction reduction of 60.4 percent and was stable to temperature below -16° C.

#### EXAMPLE 6

Into a 250 ml., four-necked flask equipped with a stirrer, thermometer, reflux condenser and gas inlet tube was charged 50 grams isodecylmethacrylate, 41 grams ethylene glycol, 62 grams water and 2.5 grams TRITON GR-5. The reaction mixture was purged for one hour with nitrogen and heated to 60° C. Then 0.015 grams of potassium persulfate was added and the reaction allowed to proceed for three hours at 60° to 70° C. The resulting emulsion was stable and had no coagulum. The emulsion gave a friction reduction of 55.5 percent and was stable to temperatures below -9° F.

#### EXAMPLE 7

Into a 250 ml., four-necked flask equipped with a stirrer, thermometer, reflux condenser and gas inlet tube was charged 50 grams isodecylmethacrylate, 56.5 grams ethylene glycol, 46.5 grams water and 2.5 grams TRITON GR-5. The reaction mixture was purged for one hour with nitrogen and heated to 60° C. Then 0.015 grams potassium persulfate was added and the reaction allowed to proceed for three hours at 60° to 70° C. The result was a stable emulsion which had a small amount of coagulum. This emulsion was stable at temperatures below -43° F.

#### EXAMPLE 8

Into a one liter, four-necked flask equipped with a stirrer, thermometer, reflux condenser and gas inlet tube was charged 200 grams of isodecylmethacrylate, 162 grams ethylene glycol, 162 grams water and 10 grams of TRITON GR-5. The reaction mixture was purged for one hour with nitrogen and heated to 60° C. Then 0.06 grams of potassium persulfate was added and the reaction allowed to proceed for three hours. The resulting emulsion was stable and had no coagulum. The emulsion was then subjected to three twenty-four hour freeze-thaw cycles ranging from -30° to +70° F. The emulsion remained stable during these freeze-thaw cycles and gave a friction reduction of 65 percent.

#### EXAMPLE 9

Into a large reactor fitted with a stirrer, thermometer, reflux condenser and a gas inlet tube was charged 70.35 pounds of isodecylmethacrylate, 56.27 pounds ethylene glycol, 56.27 pounds distilled water and 0.018 pounds of sodium ethylene diamine tetraacetic acid. The reaction mixture was purged with nitrogen for one and one-half hours and heated to 60° C. Then 0.018 pounds of potassium persulfate was added and the

reaction allowed to proceed for five hours at a temperature between 60° and 70° C. The result was a stable emulsion with no coagulum. The emulsion gave a friction reduction of 65 percent.

#### EXAMPLE 10

Into a one liter, four-necked flask equipped with a stirrer, thermometer, reflux condenser and gas inlet tube was charged 190 grams of isodecylmethacrylate, 10 grams of dimethyl diallyl ammonium chloride, 2.5 grams of TRITON X-305 (a nonionic surfactant), 7.5 grams of ALACSAN (a cationic surfactant), and 465 grams of water. The reaction mixture was then purged with nitrogen for one and one-half hours and the temperature raised to 60° C. Then 0.06 grams of potassium persulfate was added and the polymerization allowed to proceed for three hours at a temperature of about 75° C. The reaction mixture was then cooled to room temperature and the ethylene glycol was added so that the resulting polymer emulsion was about 30 percent by weight glycol. This emulsion was then subject to a freeze-thaw test. The test was three cycles ranging from a temperature of -30° F to +70° F. The emulsion was very stable and there was no phase separation at the end of the freeze-thaw test. This emulsion gave a friction reduction of 69 percent as compared to 36 percent for polyisobutylene and 64 percent for polyisodecylmethacrylate.

#### EXAMPLE 11

Into a one liter, four-necked flask equipped with a stirrer, thermometer, reflux condenser, and gas inlet tube was charged 190 grams of isodecylmethacrylate, 10 grams of diacetone acrylamide, 10 grams of sodium lauryl sulfate, and 440 grams of water. The reaction mixture was then purged with nitrogen for one and one-half hours and the temperature raised to 60° C. Then 0.06 grams of potassium persulfate was added and the polymerization allowed to proceed for three hours at 75° C. The reaction mixture was then cooled to room temperature and ethylene glycol was added so that the emulsion was about 30 percent by weight ethylene glycol. This emulsion was stable after a three cycle freeze-thaw test having temperatures ranging from +30° F to +70° F. This emulsion gave 64 percent friction reduction.

In addition to the isodecylmethacrylate emulsions illustrated above, we have also prepared emulsions of other acrylates and methacrylates in a manner similar to those described in Examples 1 to 11 above. Among the different acrylates and methacrylates which have been found to be useful in our invention and which we have used to prepare emulsions are: 2 ethylhexyl acrylate, tridecyl methacrylate, lauryl acrylate, lauryl methacrylate, stearyl acrylate and stearyl methacrylate. The emulsions of these compounds all give a friction reducing effect in hydrocarbon fluids.

The friction reduction properties of the emulsion of our invention were determined in a hydrocarbon fluid which was pumped from a container through a standard section of pipe and back into the container. This type of equipment is called a friction loop. The pressure drop in the pipe is continually measured and recorded. The pressure drop refers to the loss or drop in pressure due to the friction of the fluid flowing through a conduit at a given velocity. The loss is measured by the difference in pressure between any two given points along the conduit divided by the distance between the two points. The friction reduction is a measure in the change in pressure drop due to the use of an additive. It is the decrease in the pressure differential required to move the same fluid through the same distance of the same pipe at the same velocity. The percent friction reduction is expressed by the formula

$$\left( \frac{\Delta Pu - \Delta Pa}{\Delta Pu} \right) (100)$$

where " $\Delta Pu$ " is the pressure drop per unit length of pipe caused by the friction of the untreated base fluid and where " $\Delta Pa$ " is the pressure drop per unit length of pipe caused by the friction of the base fluid with additive. Thus, the higher the number, the more effective the friction reducing characteristics of the emulsion.

There is no reason to believe that there is a minimum molecular weight which must be achieved by the polymer in order to show friction reducing properties. A low molecular weight polymer will have a slight effect when compared to a high molecular weight polymer. However, for all practical purposes, it may be said that the polymer should have a molecular weight of at least 1,000,000. Similarly, there is no reason to believe that there is a minimum quantity which must be used to achieve a friction reducing effect. A small amount will have a slight effect. But for practical purposes a minimum of 50 ppm based on total weight of hydrocarbon fluid is necessary. The maximum amount used will largely be determined by economic considerations. However, concentrations greater than 1,000 ppm will seldom, if ever, be used. In the majority of cases, a concentration in the neighborhood of 200 to 500 ppm will produce a commercially significant effect. The friction reduction values for the emulsions of our invention given in the examples were determined at a concentration of 400 ppm based on active polymer and total weight of hydrocarbon fluid, which was kerosene.

We have also found an effective method of using the emulsions of our invention in hydrocarbon liquids without having to first isolate the polymer from the emulsion. Our method comprises adding the emulsion and hydrocarbon fluid together then adding to this mixture an alcohol such as isopropanol or methanol. The alcohol causes the polymer to be transferred from the aqueous phase to the hydrocarbon phase. The emulsion may be an aqueous emulsion of polymer and water or it may be an emulsion of polymer in the water/glycol cosolvent system. Our method can also be practiced by adding the polymer emulsion and a hydrocarbon/alcohol mixture together. In addition, our method may be practiced by simultaneously adding together the polymer emulsion, the hydrocarbon fluid, and the alcohol. In practicing any one of the above variations of our method, it must be remembered that the time of adding the alcohol is critical. The alcohol should not be added to the emulsion prior to the time when the emulsion and hydrocarbon fluid are mixed. We have also found that the weight ratio of alcohol to polymer is a critical factor in using the method of our invention. When adding the polymer emulsion and hydrocarbon fluid together, it is necessary to keep the ratio of alcohol to emulsion between 1:2 and 5:1. The ratio of alcohol to emulsion determines the speed and efficiency of the transfer of the polymer from the emulsions to the hydrocarbon fluid. The maximum ratio may be increased to values greater than 5:1 without having any deleterious effect on the invention. However, we have found that for all practical purposes, no advantage is gained by using a higher ratio. Similarly, amounts smaller than the minimum ratio of 1:2 may be used. However, we have found that when these small amounts are used the transfer process is slow and inefficient. The preferred ratio of the alcohol to emulsion is from 1:1 to 4:1. The alcohols which may be used in practicing our invention may be described as lower alkyl alcohols; that is, alkyl groups of from about one to six carbon atoms. Some examples of these alcohols are methanol, ethanol, propanol, butanol, pentanol, hexanol, isopropanol, isobutanol, tertiary butanol, and the like. The preferred alcohols are methanol and isopropanol. We have also found that acetone may be used in place of the alcohol and the term lower alkyl alcohol as used herein includes acetone unless otherwise stated.

The ratio of emulsion to hydrocarbon fluid will depend upon the amount of polymer that is desired in the hydrocarbon fluid and the concentration of polymer in the emulsion. For example, if it is desired to have the hydrocarbon fluid contain 0.5 percent by weight polymer and the emulsion contains 20 percent by weight polymer, then the weight ratio of emul-

sion to hydrocarbon fluid would be 2.5:99.5. Similarly, if it is desirable to have a hydrocarbon fluid containing 10 percent by weight polymer and the emulsion is 40 percent by weight polymer, then the weight of emulsion to hydrocarbon fluid would be 25:90. Finally, for example, if it is desirable to have a hydrocarbon fluid containing 10 percent by weight polymer and the emulsion contains 20 percent by weight polymer, then the ratio of emulsion to hydrocarbon fluid would be 50:90.

The following examples illustrate the method of our invention.

#### EXAMPLE 12

Into one holding container was placed 100 grams of a 33 percent by weight polyisodecylmethacrylate emulsion (100 ml.). Into another holding container was placed 383 grams of kerosene (480 ml.) and 67 grams of isopropanol (86 ml.). The solutions were pumped from the holding container at a ratio of 5.6 ml. of the kerosene/isopropanol mixture to 1 ml. of the emulsion into a static mixer such as described in U.S. Pat. Nos. 2,894,732; 3,051,452; 3,051,453; 3,182,965; 3,195,865; 3,206,170. As the mixture passed through the static mixture the polyisodecylmethacrylate was transferred from the aqueous phase to the kerosene. The kerosene effluent was a very viscous solution containing about 8 percent by weight polyisodecylmethacrylate.

#### EXAMPLE 13

Using the procedure described in Example 3, an emulsion was prepared comprising 400 grams of polyisodecylmethacrylate, 800 grams water and 20 grams of sodium lauryl sulfate. Then 14.4 parts of the emulsion was placed in 250 parts of kerosene and 25 parts of isopropanol was added. This mixture was stirred for several minutes with a mechanical agitator. The polyisodecylmethacrylate was transferred from the aqueous phase to the kerosene and the result was a viscous kerosene solution containing 0.2 percent by weight polymer.

#### EXAMPLE 14

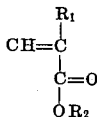
An emulsion comprising 33 percent by weight polyisodecylmethacrylate in the cosolvent of ethylene glycol and water was prepared in a manner similar to the one described in Example 1. Then 9 parts of the emulsion were added to 250 parts of kerosene and then 20 parts of isopropanol were added to the mixture. The mixture was stirred for several minutes and the polyisodecylmethacrylate was transferred into the kerosene. The result was a kerosene solution containing 0.12 percent by weight polymer.

#### EXAMPLE 15

About 13 parts of an emulsion as in Example 1 were mixed with 250 parts of kerosene. Then 40 parts of isopropanol were added and the mixture agitated for several minutes. The result was a viscous kerosene solution containing about 0.2 percent by weight polymer.

We claim:

1. An improved process for fracturing an earth formation penetrated by a well comprising injecting a hydrocarbon fracturing fluid down the well into the earth formation under pressure to cause fracturing of the earth formation wherein the improvement comprises treating the hydrocarbon fracturing fluid prior to injection with an aqueous polymer emulsion comprising (a) from 20 to 60 percent by weight of a polymer of



where "R<sub>1</sub>" is H or CH<sub>3</sub> and "R<sub>2</sub>" is an alkyl group of eight to 18 carbon atoms, (b) from 10 to 50 percent by weight glycol, (c) from 10 to 60 percent by weight water, and (d) from 1 to 10 percent by weight surfactant, said polymer emulsion being added in an amount such that the treated hydrocarbon fluid contains from about 50 p.p.m. to 1,000 p.p.m. of polymer based on the total weight of the hydrocarbon fluid.

2. A process as in claim 1 wherein the glycol is ethylene glycol.

3. A process as in claim 1 wherein "R<sub>1</sub>" is CH<sub>3</sub> and "R<sub>2</sub>" is an isodecyl group.

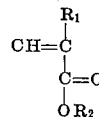
4. A process as in claim 1 wherein the polymer is a copolymer of up to about 10 percent by weight of a dialkyl diallyl ammonium chloride and isodecylmethacrylate.

5. A process as in claim 4 wherein the dialkyl diallyl ammonium chloride is dimethyl diallyl ammonium chloride.

6. A process as in claim 1 wherein the polymer is a copolymer of up to about 10 percent by weight of an acrylamide and isodecylmethacrylate.

7. An improved process for fracturing an earth formation penetrated by a well comprising injecting a hydrocarbon fracturing fluid down the well into the earth formation under pressure to cause fracturing of the earth formation wherein the improvement comprises treating the hydrocarbon fracturing fluid prior to injection with an aqueous polyisodecylmethacrylate emulsion comprising (a) from 25 to 50 percent by weight polyisodecylmethacrylate, (b) from 15 to 40 percent by weight ethylene glycol, (c) from 20 to 50 percent by weight water, and (d) from 1 to 5 percent by weight surfactant, said polyisodecylmethacrylate emulsion being added in an amount such that the treated hydrocarbon fluid contains from about 200 p.p.m. to 500 p.p.m. of polyisodecylmethacrylate polymer based on the total weight of the hydrocarbon fluid.

8. The process of reducing frictional pressure loss in hydrocarbon fluids flowing through a conduit comprising adding to said hydrocarbon fluid an aqueous polymer emulsion comprising (a) from 20 to 60 percent by weight of a polymer of



where "R<sub>1</sub>" is H or CH<sub>3</sub> and "R<sub>2</sub>" is an alkyl group of eight to 18 carbon atoms, (b) from 10 to 50 percent by weight glycol, (c) from 10 to 60 percent by weight water, and (d) from 1 to 10 percent by weight surfactant, said polymer emulsion being added in an amount such that the resulting hydrocarbon fluid contains from about 50 p.p.m. to 1,000 p.p.m. of active polymer based on the total weight of the hydrocarbon fluid.

9. A process as in claim 8 wherein the glycol is ethylene glycol.

10. A process as in claim 8 wherein "R<sub>1</sub>" is CH<sub>3</sub> and "R<sub>2</sub>" is an isodecyl group.

11. A process as in claim 8 wherein the polymer is a copolymer of up to about 10 percent by weight of an acrylamide and isodecylmethacrylate.

12. A process as in claim 8 wherein the polymer is a copolymer of up to about 10 percent by weight of dimethyl diallyl ammonium chloride and isodecylmethacrylate.

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