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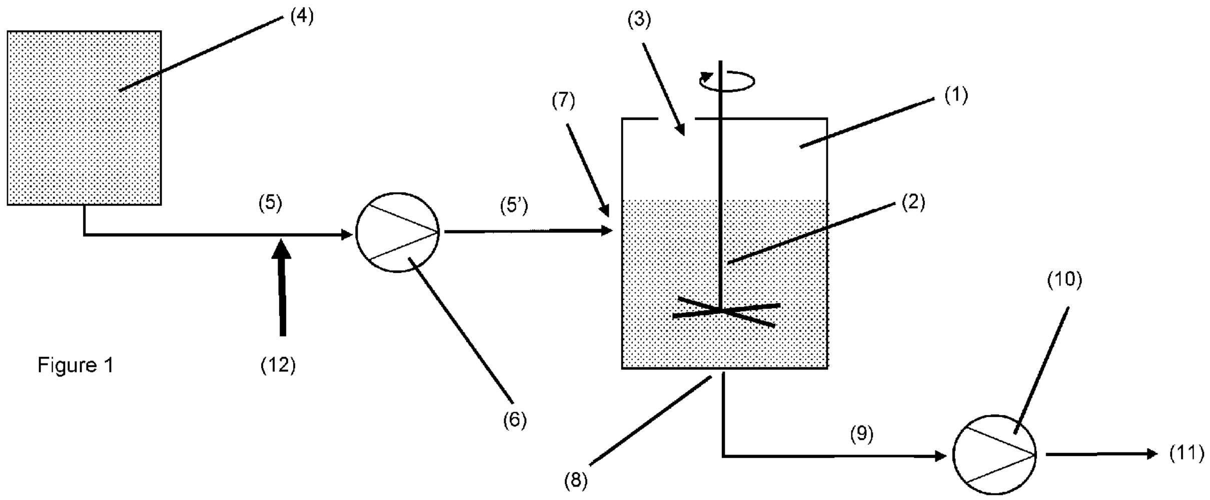

Figure 1

(57) Abstract: Device and a process for making aqueous treatment fluids comprising water-soluble polymers, preferably polyacrylamides, by mixing an aqueous base fluid with an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer to a stream of a aqueous base fluid at the suction side of a mixing vessel for mixing such fluids.

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PROCESSES AND DEVICES FOR MAKING AQUEOUS WELLBORE TREATING FLUIDS

The present invention relates to a device and a process for making aqueous treatment fluids comprising water-soluble polymers, preferably polyacrylamides, by mixing an aqueous base fluid with an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer to a stream of a aqueous base fluid at the suction side of a mixing vessel for mixing such fluids.

Aqueous wellbores treating fluids for treating wellbores are known in the art. Examples comprise fluids for fracturing, acidizing, or enhanced oil recovery. They often comprise water-soluble polymers as component. Such polymers may serve, for example, as thickeners or as friction reducers. Examples of common water-soluble polymers comprise polyacrylamides which may for example by used as thickener and/or as friction reducer for fracturing fluids.

For making aqueous treatment fluids the components thereof are mixed with water or aqueous fluids comprising water. It is known in the art to use polymers, in particular polyacrylamides as powders or as inverse emulsions.

Powders may be added as such, however, they are preferably pre-dissolved in water, thereby obtaining a diluted aqueous solution and the diluted aqueous solution used for mixing with the other ingredients. For dissolving powders of water-soluble polymers in water for oilfield applications, a large number of different processes are known in the art, for example the processes described for example in WO 2008/107492 A1, WO 2008/081048 A2, WO 2008/071808 A1, WO 2010/020698 A2, or in US 2013/0292122 A1. FR 3 063 230 A1 discloses a two-step process for dissolving polyacrylamide powders: In the first step, a polyacrylamide powder is dissolved yielding a concentrate having a polyacrylamide concentration from 0.3 wt. % to 2 wt. %. In a second step, the solution is diluted with water to a final concentration from 0.025 wt. % to 0.5 wt. % by means of a static mixer.

Processes of using inverse emulsions, in particular as friction reducers are disclosed for example in US 8,841,240 B2, US 9,315,722 B1, US 2012/0214714 A1, US 2015/0240144 A1, US 2017/0121590 A1, WO 2016/109333 A1, or WO 2017/143136 A1.

It is also known, to use powder slurries of suitable polymers as friction reducers.

Polyacrylamides may be manufactured by adiabatic polymerization of an aqueous solution comprising acrylamide and optionally further comonomers such as acrylic acid or ATBS, thereby obtaining a solid polymer gel. Such gel may be dried after polymerization, thereby obtaining a polyacrylamide powder. For use in oilfield applications, it needs to be dissolved in aqueous fluids as described above.

It is also known in the art, to dissolve the polymer gel in water, thereby obtaining directly an aqueous polyacrylamide solution for use for examples in US 4,605,689. Such a process can be carried out on-site, i.e. at the site where polyacrylamide solutions are needed. WO 2019/081318 A1, WO 2019/081319 A1, WO 2019/081320 A1, WO 2019/081321 A1, WO 2019/081323 A1, WO 2019/081327 A1, and WO 2019/081330 A1 disclose different methods of manufacturing aqueous polyacrylamide solutions on-site in modular plants.

Our older application PCT/EP2019/078218 discloses a method for producing an aqueous polyacrylamide concentrate, having a concentration from 1.0 to 14.9 wt. %, preferably from 3.1 wt. % to 7 wt. % of polyacrylamides, relating to the total of all components of the aqueous polyacrylamide concentrate. The concentrate is manufactured by adiabatic gel polymerization of a monomer solution comprising 15 to 50 wt. % of acrylamide and optionally further mono-ethylenically unsaturated monomers, followed by comminuting the gel, mixing it with water, thereby obtaining the abovementioned concentrate and transporting it to the location of use. The concentrate may be used as friction reducer for hydraulic fracturing. The application also briefly mentions that aqueous fracturing fluids may be obtained by mixing an aqueous base fluid, proppants, the aqueous polyacrylamide concentrate, and optionally further components with each other by means of a customary blender, but it provides no details about such a process.

Our older application PCT/EP2019/078211 discloses a process of fracturing subterranean formations, wherein the fracturing fluid is prepared by mixing at least an aqueous base fluid, a homogeneous aqueous polyacrylamide concentrate having a concentration of 3.1 to 10 % by weight of polyacrylamides, relating to the total of all components of the homogeneous aqueous polyacrylamide concentrate, and a proppant. The application also mentions blenders for mixing the components of the fracturing fluid. It furthermore mentions, that the concentrates may be metered into such blenders “in the same manner as inverse emulsions or aqueous solutions”. In another embodiment, the homogeneous aqueous polyacrylamide concentrates are added into the pipe which transports the aqueous fracturing fluid before or after the blender.

Blenders for making fracturing fluids are known in the art. A brief description of a blender system may for example be found in *“Flexible Blender Systems Customized for Successful Fracking Operations”,* John Callihan, Upstream Pumping, Nov. 11, 2015, Cahaba Media Group. Typically, blenders pull in water from a water source, for example from tanks, by means of a suction pump, and the water is introduced into a mixing vessel. The mixing vessel typically is open at its upper end and it is often also designated as “mixing tub” or “blender tub”. The mixing vessel mixes the water with proppant that may be delivered to the mixing tub by sand screws. Additional chemicals can also be delivered to the mixing tub. A discharge pump then pulls the mixture from the mixing tub and discharges it to the fracture pump(s) which injects the fracturing fluid into the wellbore at a pressure sufficient to generate fractures or fissures in the formation. A typical mixing tub has a volume of about 6 to 12 barrels (0.95 to 1.9 m^3) and the amount of water flowing through the mixing tub may be from

80 to 100 barrels per minute (12.7 m^3 / min – 15.9 m^3 / min). Typical hoses or pipes for transporting water or the fracturing fluid have a diameter of about 4 inches (about 0.1 m).

It was an object of the present invention to provide an improved process for making aqueous wellbore treating fluids comprising water-soluble polymers using aqueous concentrates of the water-soluble polymers as starting material.

Accordingly, the present invention relates to a device for making aqueous treatment fluids comprising water-soluble polymers comprising at least

- a mixing vessel (1) comprising at least
  - an inlet (7) for an aqueous base fluid,
  - an inlet (3) for adding treatment fluid additives,
  - means (2) for mixing the contents of the mixing vessel, and
  - an outlet (8) for the aqueous treatment fluid,
- at least one source (4) for the aqueous base fluid,
- a suction pump (6), whose inlet side is connected with the source(s) (4) for the aqueous fluid by at least one first input tube (5), and whose pressure side is connected with the inlet (7) of the aqueous mixing vessel (1) by at least one second input tube (5'),
- a discharge pump (10), whose inlet side is connected with the outlet (8) by a discharge tube (9) and whose pressure side is connected with a product tube (11) which transfers the aqueous treatment fluid to a device for further handling or use,

wherein the device additionally comprises at least one inlet (12) for an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate, which is arranged at

- at least one of the first input tube(s) (5), and/or
- at least one of the second input tube(s) (5').

In another embodiment, the invention relates to a process for making an aqueous treatment fluid comprising water-soluble polymers for treating subterranean formations by means of a device comprising at least

- a mixing vessel (1) comprising at least
  - an inlet (7) for an aqueous base fluid,
  - an inlet (3) for adding treatment fluid additives,
  - means (2) for mixing the contents of the mixing vessel, and

    - an outlet (8) for the aqueous treatment fluid,

- at least one source (4) for the aqueous base fluid,
- a suction pump (6), whose inlet side is connected with the source(s) (4) for the aqueous fluid by at least one first input tube (5), and whose pressure side is connected with the inlet (7) of the aqueous mixing vessel (1) by at least one second input tube (5'),
- a discharge pump (10), whose inlet side is connected with the outlet (8) by a discharge tube (9) and whose pressure side is connected with a product tube (11) which transfers the aqueous treatment fluid to a device for further handling or use,

wherein the device additionally comprises at least one inlet (12) for an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate, which is arranged at

- at least one of the first input tube(s) (5), and/or
- at least one of the second input tube(s) (5'),

and wherein the process comprises at least the following steps:

(I) Continuously pumping a stream of an aqueous base fluid from the source(s) (4) through the input tube(s) (5) by means of the suction pump (6),

(II) continuously adding a stream of the aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate through the at least one inlet (11) to the stream of aqueous base fluid into

- at least one of the first input tube(s) (5), and/or
- at least one of the second input tube(s) (5'),

thereby obtaining a stream of a mixture of the aqueous base fluid and the aqueous polymer concentrate,

(III) introducing the obtained mixture into the mixing vessel (1) through the inlet (7), and mixing the components by means of the mixing means (2), thereby obtaining an aqueous treatment fluid,

(IV) continuously removing a stream of the aqueous treatment fluid from the mixing vessel (1) by means of the discharge pump (10) through the outlet (8) and the discharge tube (9) and transferring it into the product tube (11).

List of figures:

With regard to the invention, the following should be stated specifically:

In the process according to the present invention, an aqueous treatment fluid for treating subterranean formations is prepared, which comprises at least one water-soluble polymer. The staring material for the process is an aqueous polymer aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate which is mixed at least with an aqueous fluid by means of a device as will be described below, thereby obtaining an aqueous treatment fluid.

Water-soluble polymers

The water-soluble polymers comprise monoethylenically unsaturated, water-soluble monomers, such as for example acrylic acid or salts thereof or acrylamide. It is not necessary that the water-soluble monomers to be used are miscible with water without any gap. In general, the solubility of the water-soluble monomers in water at room temperature should be at least 50 g/l, preferably at least 100 g/l.

Preferably, the water-soluble polymers are polyacrylamides. The term “polyacrylamide” as used herein means water-soluble polymers comprising at least 10 %, preferably at least 20 %, and more preferably at least 30 % by weight of acrylamide, wherein the amounts relate to the total amount of all monomers relating to the polymer. Polyacrylamides include homopolymers and copolymers of acrylamide and other monoethylenically unsaturated comonomers. Polyacrylamide copolymers are preferred.

Examples of water-soluble, monoethylenically unsaturated monomers comprise neutral monomers such as acrylamide, methacrylamide, N-methyl(meth)acrylamide, N,N’-dimethyl(meth)acrylamide, N-methylol(meth)acrylamide or N-vinylpyrrolidone. Further examples comprise anionic monomers, in particular monomers comprising -COOH groups and/or $-SO_3H$ groups are salts thereof such as acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid or fumaric acid or salts thereof. Examples of monomers comprising $-SO_3H$ groups or salts thereof include vinylsulfonic acid, allylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid (ATBS), 2-methacrylamido-2-methylpropanesulfonic acid, 2-acrylamidobutanesulfonic acid, 3-acrylamido-3-methylbutanesulfonic acid or 2-acrylamido-2,4,4-trimethylpentanesulfonic acid. Preference is given to 2-acrylamido-2-methylpropanesulfonic acid (ATBS) or salts thereof.
Preferred monomers comprising acidic groups comprise acrylic acid and/or ATBS or salts thereof.

Further examples of monomers comprise water-soluble, monoethylenically unsaturated monomers comprising cationic groups. Suitable cationic monomers include especially monomers having ammonium groups, especially ammonium derivatives of N-(ω-aminoalkyl)(meth)acrylamides or ω-aminoalkyl (meth)acrylates such as 2-trimethylammoniooethyl acrylate chloride $H_2C{=}CH\text{-}CO\text{-}CH_2CH_2N^+(CH_3)_3\,Cl^-$ (DMA3Q). Furthermore, associative monomers may be used. Examples of associative monomers have been described for example in WO 2010/133527, WO 2012/069478, WO 2015/086468 or WO 2015/158517.

Besides water-soluble monoethylenically unsaturated monomers, also water-soluble, ethylenically unsaturated monomers having more than one ethylenic group may be used. Monomers of this kind can be used in special cases in order to achieve easy crosslinking of the polymers. The amount thereof should generally not exceed 2% by weight, preferably 1% by weight and especially 0.5% by weight, based on the sum total of all the monomers. More preferably, the monomers to be used in the present invention are only monoethylenically unsaturated monomers.

The specific composition of the polymers may be selected according to the desired use of the polymers.

Preferred polymers are polyacrylamides and comprise, besides at least 10 % by weight, preferably at least 20 % by weight and for example at least 30 % by weight of polyacrylamide, one further water-soluble, monoethylenically unsaturated monomer, preferably at least one further monomer selected from the group of acrylic acid or salts thereof, ATBS or salts thereof, or associative monomers. In certain embodiments, the polyacrylamides comprise from 50 to 95 wt. % of acrylamide and from 5 to 50 wt. % of ATBS and/or acrylic acid or salts thereof.

The weight average molecular weight M_w of the water-soluble polymer, in particular the water-soluble polyacrylamides is selected by the skilled artisan according to the intended use of the polyacrylamides. For many applications high molecular weights are desirable. A high molecular weight corresponds to a high intrinsic viscosity (IV) of the polyacrylamides. In one embodiment of the invention, the intrinsic viscosity may be at least 15 deciliter/gram (dL/g). In one embodiment of the invention, the intrinsic viscosity is from 30 to 45 dl/g. The numbers mentioned relate to the measurement with an automatic Lauda iVisc® LMV830 equipped with an Ubbelohde capillary tube and automatic injection. For the measurements an aqueous solution of the polymers to be analyzed was prepared having a concentration of 250 ppm. The pH was adjusted at 7 by means of a buffer and the solution comprised additionally 1 mol /l of NaCl. Further four dilutions were done automatically. The viscosity at five different concentrations was measured at 25 °C. The IV value [dL/g] was determined in usual manner by extrapolating the viscosities to infinite dilution. The error range is about +/- 2 dL/g.

<u>Aqueous polymer concentrate</u>

The aqueous polymer concentrates to be used in the process according to the present invention comprises at least a water-soluble polymer, preferably a polyacrylamide, more preferably a polyacrylamide copolymer as described above and an aqueous liquid.

The aqueous liquid comprises water. The term “water” includes any kind of water such as desalinated water, fresh water or water comprising salts, such as brines, sea water, formation water, produced water or mixtures thereof. Besides water, the aqueous liquid may comprise organic solvents miscible with water, however the amount of water relating to the total of all solvent should be at least 70 % by weight, preferably at least 90 % by weight, more preferably at least 95 % by weight. In one preferred embodiment, the aqueous liquid comprises only water as solvent.

The aqueous polymer concentrates to be used for making aqueous treatment fluids according to the present invention are homogeneous. The term should be understood as “substantially homogeneous”, so minor variations of polymer density or polymer concentration within a concentrate may be possible. However, polyacrylamide dispersions in oil or water-in-oil emulsions of polyacrylamide are heterogeneous products (which comprise at least to different phases) are not subject of the process according to the present invention.

The concentration of the water-soluble polymers, preferably of the polyacrylamides in the aqueous polymer concentrate is from 1 to 10 wt. % relating to the total of all components of the polymer concentrate, in particular from 2 to 10 wt. %, preferably from 2.5 to 10 wt. % or from 2.5 to 8 wt. % and for example from 3.1 to 7 wt. %.

Keeping the concentration and the molecular weights of the water-soluble polymer, preferably the polyacrylamides to be used in mind, the aqueous polymer concentrates typically may be identified as (soft) solids or viscous solutions. The aqueous polymer concentrates are pumpable.

The aqueous polymer concentrate preferably has a viscosity of at least 1,000 mPas*s, measured at 10 s^{-1}, for example at least 1,000 mPas*s, preferably at least 5,000 mPas*s, more preferably at least 10,000 mPas*s. As a rule, its viscosity should not exceed 500,000 mPa*s, preferably not 300,000 mPa*s. In one embodiment, the viscosity of the aqueous polymer concentrate is from 1,000 mPa*s to 500,000 mPa*s, preferably from 5,000 mPa*s to 300,000 mPa*s, for example from 10,000 mPa*s to 100,000 mPa*s. Said viscosities relate to a measurement by means of a rotational rheometer having a plate-plate geometry (DHR-1 of TA Instruments, plate diameter Ø 40 mm, h = 1mm, deformation 10 %) and a measuring temperature of 23°C.

The aqueous polymer concentrates, preferably the aqueous polyacrylamide concentrates to be used for the method according to the present invention basically may be manufactured by any technology.

In one embodiment of the invention, the aqueous polymer concentrates may be obtained by mixing water-soluble polymers as described above with an aqueous liquid. The term “aqueous liquid” has already been defined above. Basically, any kind of mixing unit capable of mixing solids with liquids may be used. For example, extruder or kneaders may be used. In one embodiment of the invention, a kneader may be used for mixing. Examples of suitable kneaders are disclosed in WO 2006/034853 A1 and the literature cited therein. Suitable kneaders are also commercially available.

In a preferred embodiment of the invention, the aqueous polymer concentrates may be obtained by adiabatic gel polymerization of an aqueous solution of water-soluble, monoethylenically unsaturated monomers thereby yielding an aqueous polymer gel, preferably an aqueous polyacrylamide gel, followed by comminuting the gel and mixing it with an aqueous liquid. The method of “adiabatic gel polymerization” is well known to the skilled artisan. Details are described for example in WO 2019/081318 A1 and other documents cited in the introduction. The aqueous polymer gel typically has a concentration from 15 % to 50 % by weight of water-soluble polymers, preferably from 20 wt. % to 35 wt. %, relating to the total of all components of the gel.

The aqueous polymer gel obtained by adiabatic gel polymerization is comminuted and mixed with an aqueous liquid in a second step thereby obtaining an aqueous polymer concentrate as described above. Comminution and mixing may be followed by a step of homogenization. Basically, any kind of comminution means may be used for disintegrating the aqueous polymer gel into smaller particles. Examples of suitable means for comminuting aqueous polymer gels include cutting devices such as knives or perforated plates, crushers, kneaders, static mixers or water-jets. Homogenization may be effected by simply allowing to stand a mixture of small gel pieces and aqueous liquid in a suitable vessel. It may be supported for example by pumping the mixture through a loop using circulation pumps. Optionally, the loop may comprise one or more static mixers. Further examples include tumbling, shaking or any mixing method known to skilled in the art for highly viscous liquids, for example using progressive cavity pumps.

<u>Components of the aqueous treatment fluid</u>

The aqueous treatment fluid to be manufactured according to the process according to the present invention comprises at least a water-soluble polymer, preferably a polyacrylamide as described above which is introduced in the process as aqueous polymer concentrate as also described above.

It furthermore comprises at least an aqueous base fluid. Examples of aqueous base fluids comprise fresh water, brines, sea water, formation water treated water or mixtures thereof. The salinity of the water may be -for example- from 500 ppm to 300,000 ppm total dissolved solids (TDS), for example from 1,000 ppm to 100,000 ppm.

The concentration of the water-soluble polymer, preferably the water-soluble polyacrylamides in the treatment fluid depend on the application of the treatment fluid and may be selected by the skilled artisan. It may range from 20 to 600 ppm, relating to the total of all components of the treatment fluid if the water-soluble polymers, preferably water-soluble polyacrylamides are used as friction reducers in slickwater fracturing operations. For fracturing using viscosified fracturing fluids, or for enhanced oil recovery, the concentration may be for example from 0.05 wt. % to 0.5 wt. %.

The aqueous treatment fluid may of course comprise further components. The nature and the amount of such further components depend on the intended use of the aqueous treatment fluid. Examples of such additional components comprise biocides, corrosion inhibitors, scale inhibitors, iron control agents, or clay control agents. If the treatment fluid is a fracturing fluid, at least a part of the fracturing fluid comprises a proppant. Proppants are small hard particles which cause that fractures formed in course of the process do not close after removing the pressure. Suitable proppants and suitable amounts thereof are known to the skilled artisan. Examples of proppants include naturally-occurring sand grains, resin-coated sand, sintered bauxite, glass beads, or ultra-lightweight polymer beads.

Device to be used for the process

For making aqueous treatment fluids comprising water-soluble polymers according to the process according to the present invention a device as will be described in the following is used.

One embodiment of a device according to the present invention is schematically shown in figure 1.

The device comprises at least one source (4) for the aqueous base fluid. The term “source” is intended to cover any kind of source. For example, a river, a lake or another water reservoir may serve as source (4) for the aqueous base fluid. In one embodiment, the aqueous base fluid may be provided in a pipeline to the site of use. In one embodiment, the source (4) is a tank. Of course, a plurality of sources (4) may be used, for example a plurality of tanks. Preferably, such tanks (4) are mobile, so that they can be easily relocated, for example from one oil well to another oil well. In certain embodiments of the present invention, the tanks may be tank containers, tank trailers or tank trucks. Basically, the tanks may have any shape and size. In one embodiment, tanks may be rectangular. The volume of the tanks is not limited. Mobile tanks as mentioned, may have a volume from 10 m^3 to 100 m^3, for example from 50 m^3 to 100 m^3. The tanks may also serve a buffer tanks to ensure an uninterrupted supply with the aqueous base fluid, that is to say they are simultaneously filled from a water source such as a river, a lake or another water reservoir and aqueous base fluid is withdrawn from the tank(s) for use in the process.

The device furthermore comprises at least a mixing vessel (1). Basically, the mixing vessel may have any shape and size. In certain embodiments, it has a tubular shape. Its volume may by for example be from 0.5 m^3 to 5 m^3, in particular from 0.75 m^3 to 3 m^3. The vessel preferably is mounted on a mobile platform, so that it can be easily relocated, for example from one oil well to be treated to another oil well to be treated.

The mixing vessel (1) comprises at least an inlet (7) for the aqueous base fluid, an inlet (3) for adding treatment fluid additives, and an outlet (8) for the aqueous treatment fluid. It furthermore, comprises means (2) for mixing the contents of the mixing vessel. The mixing vessel (1) may comprise a plurality of inlets (7) for the aqueous base fluid. As will be shown below, using a plurality of inlets (7) may support mixing.

The inlet (3) for treatment fluid additive basically may be any kind of inlet. The mixing vessel (1) may of course comprise a plurality of inlets (3). Its kind depends of whether liquid or solid treatment fluid additives are to be added. In one embodiment, the mixing vessel may comprise an opening at the upper side into which such additives may be added. Liquid additives may be added be means of pipes or hoses and solid additives may for example by suitable means for dosing solids, such as dosing screws or rocking conveyors.

If the treatment fluid is a fracturing fluid and it is necessary to add a proppant to at least a part of the fracturing fluid, the mixing vessel (1) typically comprises a dosing screw or a plurality of dosing screws, for example three dosing screws for adding the proppants to the aqueous base fluid through an inlet (3) at the upper side of the mixing vessel (1).

Mixing means (2) may be any kind of means suitable for mixing the contents of the mixing vessel. In one embodiment, the inlet(s) (7) for the aqueous base fluid itself function as mixing means (2). In this embodiment, the mixing vessel (1) preferably comprises a plurality of inlets (7). The stream aqueous base fluid is introduced into the mixing vessel (1) through the inlet(s) (7) at a velocity capable of creating turbulences in the mixing vessel (1) which serve to mix the contents of the mixing vessel (1). In order to increase the velocity of the streaming aqueous base fluid, in one embodiment, the inlet(s)(7) may be connected with orifices. In other embodiments, the mixing vessel (1) may be equipped with a stirrer (2) as indicated in figure 1. Of course, both embodiments may be combined, i.e. the contents of the mixing vessel (1) is mixed by means of introducing the aqueous base fluid and by means of an additional stirrer.

The transfer of the aqueous base fluid from the source(s) (4) to the mixing vessel (1) is effected by means of a suction pump (6), whose inlet side is connected with the source(s) (4) for the aqueous fluid by at least one first input tube (5), and whose pressure side is connected with the inlet (7) of the mixing vessel (1) by at least one second input tube (5').

In one embodiment of the invention, the device comprises a plurality of first input tubes (5) which are connected with the inlet side of the suction pump (6). The other end of the first input tubes are connected with a number of sources (4), in particular a number of tanks. Such an embodiment is schematically shown in figure 2.

The term “tube” as used throughout this invention, encompasses rigid tubes such as pipes or pipelines as well as flexible tubes, such as for example hoses or flexible metal tubes. A tube may of course comprise both, rigid and flexible sections. The diameter of the tubes may be for example from 5 cm to 15 cm. Tubes used in oilfield applications often have a diameter of about 10.2 cm (4 inches).

Removing the contents of the mixing vessel is effected by means of a discharge pump (10), whose inlet side is connected with the outlet (8) of the mixing vessel (1) by a discharge tube (9) and whose pressure side is connected with a product tube (11) which transfers the aqueous treatment fluid to a device for further handling or use. The product tube (11) may for example transfer the aqueous treatment fluid to high pressure pumps for injecting the aqueous treatment fluid into a subterranean formation.

According to the present invention, the device furthermore comprises at least an inlet (12) for an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate. Details of such a concentrate have already been described above. The inlet (12) or a plurality of such inlets (12) is arranged at

- at least one of the first input tube(s) (5), and/or
- at least one of the second input tube(s) (5’).

Several embodiments of adding the aqueous polymer concentrate into the first input tube (5) are schematically represented in figures 1 to 4, and one embodiment of adding the aqueous polymer concentrate into the second input tube (5’) is schematically represented in figure 9.

If there is a plurality of first input tubes (5), also more than one of the first input tubes (5) may comprise an inlet (12). Furthermore, a single first input tube (5) may comprise a plurality of inlets (12). Accordingly, if there is a plurality of second input tubes (5’), also more than one of the second input tubes (5’) may comprise an inlet (12). Furthermore, a single second input tube (5’) may comprise a plurality of inlets (12).

In one embodiment of the invention, the inlet(s) (12) are arranged at least at one of the first input tube(s) (5) and the aqueous polymer concentrate is added through the inlet(s) (12) into at least one of the first inlet tube(s) (5). Adding the aqueous polymer concentrate into the first input tube(s) (5) provides the advantage, that the mixture of aqueous base fluid and the aqueous polymer concentrate passes through the suction pump (6) before it enters into the mixing vessel (1). Said passage through the suction pump supports dispersing the aqueous polymer concentrate in the aqueous base fluid.

In another embodiment of the invention, the inlet(s) (12) are arranged at least at one of the second input tube(s) (5’) and the aqueous polymer concentrate is added through the inlet(s) (12) into at least one of the second inlet tube(s) (5’). In that embodiment, the mixture of aqueous base fluid and the aqueous polymer concentrate does not pass through the suction pump (6) before it enters into the mixing vessel (1). Nevertheless, also the passage through the second inlet tube(s) (5’) supports dispersing the aqueous polymer concentrate in the aqueous base fluid.

The aqueous polymer concentrate may be stored in a suitable container (13), for example a tank, tank container, tank trailer or tank truck for use in the process according to the present invention. From the container (13) it may be provided to the inlet(s) (12) in the first input tube(s) (5) and/or to the second input tube(s) (5’) by means of a pump (14) through a tube. The tube may for example have a diameter of about 5.1 cm (2 inches). An embodiment in which the inlet (12) is arranged at the first inlet tube (5) is schematically shown in figure 3.

In one embodiment of the invention, the aqueous polymer concentrate is added into the first input tube(s) (5) or the second input tube(s)(5’) through one single inlet (12) per tube. Such a single inlet (12) may have a diameter of about 5.1 cm (2 inches), if the first input tube (5) or the second input tube(s)(5’) have a diameter of about 10.2 cm (4 inches).

In another embodiment of the invention, the aqueous polymer concentrate is added into the first input tube(s) (5) and/or the second input tube(s)(5’) through a plurality of inlets (12) per input tube. An embodiment, in which the inlets (12) are arranged at the first input tube (5) is schematically shown in figure 4. Such an embodiment has the advantage, that the total amount to be added is distributed over a larger number of inlets, so that the diameter of the inlets (12) can be reduced. Strings of aqueous polymer concentrates having a lower diameter are easier to dissolve in the aqueous base fluid than strings having a larger diameter. The number of inlets may be selected by the skilled artisan according to his/her needs. In this embodiment, for example the number of inlets (12) may be from 5 to 100, for example from 5 to 50 or from 5 to 15 per tube without wishing the invention to limit to these numbers. Staying with the example above, for adding an aqueous polymer concentrate to a stream of aqueous base fluid in the first input tube (5) and/or the second input tube (5’) having a diameter of about 10.2 cm (4 inches), instead of a single inlet having a diameter of about 5.1 cm (2 inches), 5 to 10 inlets (5) having a diameter of about 1.3 cm (0.5 inch) or from 10 to 20 having a diameter of about 0.65 cm (0.25 inch) may be used. Figure 5 shows such an embodiment comprising 12 inlets (12) for the aqueous polymer concentrate.

In another embodiment of the invention, the inlet (12) for the aqueous polymer concentrate is connected with a distributor (15) which is a hollow body comprising a plurality of perforations, which is arranged in the first input tube (5) and/or the second input tube (5’) and the stream of the aqueous base fluid circulates around the distributor. The hollow body may be for example a hollow cylinder or a hollow cuboid comprising perforations in the lateral area. The perforations preferably may be circular, but of course also other shapes are possible. The diameter and the number of perforations may be selected by the skilled artisan according to his/her needs. The diameter of the perforations may for example be from 1 mm to 10 mm, preferably from 1 mm to 5 mm and for example from 1.5 mm to 3 mm. For non-circular perforations, the term “diameter” refers to the longest dimension. The number of perforations may be for example from 100 to 2000. In operation, aqueous polymer concentrate is introduced through the inlet (12) into the distributor and pressed through its perforations. The formed strings of aqueous polymer concentrate are carried away by the aqueous base fluid.

One example of this embodiment is schematically shown in figures 6 and 7. The drawings show a cylindrical distributor (15) which is fixed at its lower and upper end to the input tube (5). The lateral area of the cylinder comprises perforations. Its diameter is less than the diameter of the input tube (5), so that aqueous base fluid flows around the distributor. It is the advantage of this embodiment that the distributor (15) comprises a large number of perforations, however, only one tube which provides aqueous polymer gel needs to be connected to the inlet (12).

Another example of this embodiment is schematically shown in figure 8. In this embodiment, the distributor (15) is a hollow cuboid, which is arranged in such a manner, that the narrow sides of the cuboid point in flow direction. The two broader sides of the cuboid point perpendicular to the flow direction and comprise perforations. Details of the perforations have already mentioned above and we refer to the respective passage. In operation, aqueous polymer concentrate is introduced through the inlet (12) into the cuboid distributor and pressed through its perforations. The formed strings of aqueous polymer concentrate are carried away by the aqueous base fluid.

Process for making treatment fluids

In the process for making aqueous treatment fluids comprising water-soluble polymers for treating subterranean formations a device as described above is used. The process comprises at least the process steps (I) to (IV).

In course of step (I), a stream of the aqueous base fluid is pumped continuously from the source(s) (4), preferably the tank(s) to the mixing vessel (1) by means of the suction pump (6), and the aqueous base fluid flows through the first input tube(s) (5), the suction pump (6) the second input tube(s)(5’) and the inlet(s) (7) into the mixing vessel. As already outlined above, a stream of aqueous base fluid may also be pumped through a plurality of input tubes (5).

In course of step (II), a stream of the aqueous polymer concentrate as described above is added through the at least one inlet (12) to the stream of aqueous base fluid in at least one of the first input tube(s) (5) and/or at least one of the second input tube(s)(5’), thereby obtaining a stream of a mixture of the aqueous base fluid and the aqueous polymer concentrate. Details of adding the aqueous polymer concentrate, such as numbers of inlets (12) or the use of distributors (15) have already disclosed above and we refer to the respective passages.

In course of step (III), the obtained mixture is introduced into the mixing vessel (1) through the inlet(s) (7). In the mixing vessel (1) further components may be added and all components are mixed by means of the mixing means (2), thereby obtaining an aqueous treatment fluid. Because the polymers are water-soluble they start to dissolve once the aqueous polymer concentrates are in contact with the aqueous base fluid. If the aqueous polymer concentrate is already added into the first input tube (5), the dissolution may be supported by the passage through the suction pump and then continued in the second input tube (5') and in the mixing vessel (1). In case the aqueous treatment fluids are aqueous fracturing fluids in course of step (III) proppants are added into the mixing vessel (1) at least to a part of the aqueous fracturing fluid.

In course of step (IV) a stream of the aqueous treatment fluid is continuously removed from the mixing vessel (1) by means of the discharge pump (10) through the outlet (8) and the discharge tube (9) and transferred into the product tube (11).

Because the process is a continuous process, it goes without saying that -except for the phase of starting or stopping the process- the rates of charging and discharging the mixing vessel (1) are the same. The amount of aqueous base fluid entered into the mixing vessel (1) is selected by the skilled artisan according to his/her needs. It may be for example from 10 to 20 m^3/min without wishing the invention to be limited to these numbers.

By means of the product tube (11), the aqueous treatment fluid is transferred to the location of further use, for example to a high-pressure pump for injecting the aqueous treatment fluid into a subterranean formation.

<u>Process for treating subterranean formations</u>

In another embodiment, the present invention relates to a process for treating a subterranean formation penetrated by at least a wellbore by preparing an aqueous treatment fluid comprising water-soluble polymers and injecting it into the wellbore, and wherein the aqueous treatment fluid is prepared by a process as described above.

In one embodiment, said process is a process of fracturing subterranean formations. In course of the fracturing process, the aqueous treatment fluid is injected into the wellbore at a rate and pressure sufficient to penetrate into the formation, and to initiate or extend fractures in the formation. At least a part of the aqueous treatment fluid injected additionally comprises a proppant. The proppant is added to mixing vessel as described above.

In the process of fracturing, the water-soluble polymers, in particular the aqueous polyacrylamides may serve for different purposes. In slickwater fracturing operations, the water-soluble polymers serve as friction reducers for reducing pressure losses cause by turbulences. In such applications the concentration of the water-soluble polymers, in particular the polyacrylamides may range from 20 to 600 ppm, relating to the total of all components of the treatment fluid except the proppants. For fracturing operations using viscosified fracturing fluids the concentration is higher and may be for example from 0.05 wt. % to 0.5 wt. %.

In other embodiments, the process for treating subterranean formations is a process of enhanced oil recovery. For enhanced oil recovery processes, the subterranean formation comprises at least one injection wellbore and at least one production wellbore. The aqueous treatment fluid is injected into the injection wellbore(s) are flows in the formation towards the production wellbores, thereby mobilizing crude oil which can be recovered from the production wellbore(s).

Other embodiments

In another embodiment, the present invention relates to a device and a process for making aqueous fracturing fluids. Specifically, it relates to a process for making an aqueous treatment fluid comprising water-soluble polymers for treating subterranean formations by means of a device comprising at least

- a mixing vessel (1) comprising at least
    - an inlet (7) for an aqueous base fluid,
    - an inlet (3) for adding treatment fluid additives,
    - means (2) for mixing the contents of the mixing vessel, and
    - an outlet (8) for the aqueous treatment fluid,
- at least one source (4) for the aqueous base fluid,
- a suction pump (6), whose inlet side is connected with the source(s) (4) for the aqueous fluid by at least a first input tube (5), and whose pressure side is connected with the inlet (7) by at least one second input tube (5’),
- a discharge pump (10), whose inlet side is connected with the outlet (8) by a discharge tube (9) and whose pressure side is connected with a product tube (11) which transfers the aqueous treatment fluid to a device for further handling or use,

wherein the discharge tube (9) connecting the outlet (8) with the discharge pump (10) additionally comprises at least one inlet (12) for an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate,

and wherein the process comprises at least the following steps:

(Ia) Continuously pumping a stream of aqueous base fluid by means of the suction pump (6) from the storing tank (4) through the first input tube(s) (5) and the second input tube(s)(6) and the inlet (7) into the mixing vessel (1),

(IIa) adding treatment fluid additives through the inlet (3) and mixing the components in the mixing vessel (1) by means of the mixing means (2), thereby obtaining an aqueous treatment fluid,

(IIIa) continuously removing a stream of the aqueous treatment fluid from the mixing vessel (1) through the outlet (8) into the discharge tube (9) by means of the discharge pump (10),

(IVa) continuously adding a stream of the aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate through the inlet (12) to the stream of aqueous treatment fluid in the discharge tube (9), and

(Va) transferring the aqueous treatment fluid comprising the aqueous polymer concentrate through the discharge pump (10) into the product tube (11), thereby obtaining an aqueous treatment fluid comprising water-soluble polymers.

Such an embodiment is schematically shown in figure 10. The device used for the process is very similar to the device described above, except that the inlet(s) (12) for the aqueous polymer concentrate are not located at the first input tube (5) and/or the second input tube (5') but at the discharge tube (9). The inlet(s) (12) may be as described above.
In the embodiment described in this paragraph, the aqueous polymer concentrates are added to the aqueous treatment fluid, i.e. the fluid which already contains other components, such as for example proppants. The aqueous polymer concentrate dissolves while the aqueous treatment fluid passes through the discharge pump (10) and flows through the product tube (11). Except for the location of the inlet(s) (12) for the aqueous polymer concentrate the device is the same as described above and we refer to the specification above. Also, the process is the same except as the differences mentioned in this paragraph.

The invention is illustrated in detail by the examples which follow.

Polymer concentrates used:

The manufacture of the aqueous polymer concentrate in the following is illustrated by the lab procedure. Larger amounts can be manufactured in analogously in larger plants.

Step 1:

Preparation of an aqueous gel of a copolymer comprising 69.4 wt.% (75.0 mol%) of acrylamide and 30.6 wt.% (25 mol%) of sodium acrylate stabilized with 0.25 wt.% Na-MBT relating to polymer by adiabatic gel polymerization (solids content of 23 % by weight relating to the total of the gel)

A 5 L beaker with magnetic stirrer, pH meter and thermometer was filled with 1600 g of distilled water, 702.04 g of sodium acrylate (35% by weight in water), and 1071.69 g of acrylamide (52% by weight in water). Then 10.5 g of diethylenetriaminepentaacetic acid pentasodium salt (Trilon C; 5% by weight in water), and 4 g of the stabilizer sodium 2-mercaptobenzothiazole (Na-MBT; 50% by weight in water) were added. After adjustment to pH 6.4 with sulfuric acid (20% by weight in water) and addition of the rest of the water to attain the desired monomer concentration of 23% by weight (total amount of water 1690.08 g minus the amount of water already added, minus the amount of acid required), the monomer solution was adjusted to a temperature of approx. -3 °C. The solution was transferred to a Dewar vessel, the temperature sensor for the temperature recording was inserted, and the flask was purged with nitrogen for 45 minutes. The polymerization was initiated at 0 °C with 21 g of a 10% aqueous solution of 2,2'-azobis(2-methylpropionamidine) dihydrochloride (Wako V-50; 10h $t_{1/2}$ in water 56°C), 1.75 g of *t*-butyl hydroperoxide (1% by weight in water) and 1.05 g of a 1% sodium sulfite solution. With the onset of the polymerization, the temperature rose to 54.6 °C within about 63 min. A solid polymer gel block was obtained.

After polymerization, the gel block was incubated 4 hours at 60 °C. Then, the block was cut vertically into two pieces. One part was sealed in a plastic bag for use in step 2. The other part was kept for comparative example 2.

Step 2:

Preparation of an aqueous polyacrylamide concentrate

The aqueous polyacrylamide gel obtained in course of step 1 was first chopped to small particles ranging in size from 2 to 5 mm. The chopped particles were then dispersed into a 600 ml beaker containing the desired amount of distilled water. A small amount of a water-soluble, blue dye was added in order to obtain a blue concentrate. Such a dyed concentrate allows better monitoring of the process of dissolution. The gel particles were added while mixing via an overhead mixer with a 75 mm diameter half-moon propeller. Finally, a homogeneous polymer concentrate was obtained.

For the tests, several samples having a polymer concentration from 2.7 to 3.3 wt. % of polymers relating to the total of all components of the polymer concentrate were used.

Friction Loop Apparatus

The friction reduction performance of the friction reducing agent was assessed using a Chandler model M6500 Mini-Loop which circulates fluid through a section of known diameter pipe to determine the effectiveness and longevity of a friction reducing agent added to a test fluid. Fluid in the loop flows from a ~11 l (~ 3 gallon) reservoir through a pump and a ~ 50 cm (2 feet) long section of pipe before returning to the reservoir to be recirculated. Pressure drop is measured over this section of pipe.

The friction loop was loaded with 11.34 l (3 gallons) of aqueous test fluid (fresh water or brines). The flow rate was set to ~15 l per minute (4.0 gallons per minute) and once a stable, initial pressure was recorded. Thereafter, the friction reducing composition to be tested was injected into the vortex of the fluid reservoir using a plastic syringe. The injection time was taken as the start of the test (time = 0 seconds). The subsequent drop in pressure measured the performance of the friction reducing composition

Pressure data was converted to friction reduction using the formula:

$$\%\,Friction\,Reduction\,(\%\,FR) = \frac{Initial\,Pressure\,with\,no\,FR - Pressure\,with\,FR}{Initial\,Pressure\,with\,no\,FR}$$

Friction loop tests

The tests were carried out at ambient temperatures.

For the friction loop tests, the solutions obtained from the tests with the blender already had polymer dissolved in the water. For each test, 11.34 l of this blender sample (water with dissolved polymer) were directly added to the friction loop. This is in contrast to a typical lab test, were the water is preloaded into the friction loop, and a small amount of polymer is added at the start of the test. Results are will be shown below where the percentage of friction reduction obtained after 5 min were noted.

Description of the tests

For the tests, a commercially available blender truck for mixing aqueous fracturing fluids was used, which was modified for processing the aqueous polymer concentrates as described in the present invention.

The blender consists of three primary elements: a suction pump, a mixing tub having a volume of about 12 barrels (1.9 m^3) and a discharge pump. The suction pump draws in water and feeds it to the tub. In the tub (a vessel which has openings at the upper side), water, proppants and further chemical additives are mixed. Finally, the discharge pump carries the mixture to high pressure pumps capable of the pressures and rates that enable hydraulic fracturing. Conventional friction reducers such as inverse emulsions of polyacrylamides or aqueous polyacrylamide solutions obtained by dissolution of polyacrylamide powders are usually added by means of a tube, such as a hose, having for example a diameter of about 2.54 cm (1 inch) through the opening at the upper side of the tub. Water is introduced into the tub by a plurality of inlets for water thereby causing the water in the tub to rotate clockwise. The tub comprises a stirrer which rotates counterclockwise. The tub furthermore comprises three screw conveyors for adding proppants into the tub through the opening at the upper side of the tub. For the present tests no proppant is added, in order to better monitor the dissolution of the aqueous polyacrylamide concentrate. After the discharge pump, a sampling valve is attached to the discharge lines to take samples. In the present example, the discharge pump is connected with tanks to store the manufactured fluid.

Water for use in the process is stored in a plurality of water tanks, each having a volume of about 500 barrels (about 79.5 m^3). At the suction side, the blender comprises a plurality of connections for water, which are connected with the water tanks via 4” (10.2 cm) hoses. Water was introduced into the mixing tub at a flow rate of 80 barrels per minute (12.7 m^3 / min). The aqueous polymer concentrate was introduced into the mixer a rate of about 5 gallons per minute (gpm) (0.0189 m^3/ min) or at a higher rate of about 25 gpm (0.0946 m^3/min). The exact numbers for each of the tests will be shown in table 1. The methods of adding the aqueous polyacrylamide concentrates will be explained below. Keeping the abovementioned numbers in mind, the average residence time of the mixture in the tub is short, namely only about 9 s.

<u>Adding the aqueous polymer concentrate to the water</u>

The aqueous polymer concentrate was added at the suction side of the blender into the tube providing water to the blender at a position before it enters into the suction pump. One of the connections for the hoses providing water was extended by a short rigid tube comprising inlets for the aqueous polymer concentrate. 3 different constructions were used:

1) A rigid tube having a diameter of about 4 inches (10.2 cm) comprising one single inlet having a diameter of 2 inches (5.16 cm). Such a construction will also be referred to as “tee”. The inlet was fed from an intermediate bulk container comprising the aqueous polyacrylamide concentrate by means of a gear pump.

2) In a second embodiment, the stream of aqueous polymer concentrate was split into 6 streams and the rigid tube comprised 6 inlets having a diameter of 0.5 inch (1.28 cm) each. Such a construction is also referred to as “Medusa”.

3) In a third embodiment, the stream of aqueous polymer concentrate was split into 12 streams and the rigid tube comprised 12 inlets having a diameter of 0.25 inch (0.64 cm) each. Such a construction is also referred to as “Medusa”.

For comparative purposes, the aqueous polymer concentrate was introduced through the opening at the upper side of the tub by means of a 2-inch (5.16 cm) hose. The hose did not immerse into the aqueous mixture in the tub but ended in the head space above the mixture.

The mixing in the tub was visually observed. Furthermore, samples were also taken using the valve on the discharge side. The samples were visually observed for homogeneity. The water was also poured over a screen to observe if undissolved clumps were present. This water was also tested in a friction loop to assess the performance of the polymer solution as friction reducer.

The details of the tests and the results are summarized in table 1.

No.	Injection Location	Inlet type	Aqueous polymer concentrate		Final polymer Conc. [ppm]	% friction reduction (FR) after 5 min	Blender Tub Observation	Discharge samples - observation of undissolved material
			Conc.	Flow rate [gpm / m^3/min]				
1	Suction	6 x 0.5" Medusa	2,8%	5,5 (0.0208)	45	65,1	No chunks in blender	Water looked clear
2	Suction	6 x 0.5" Medusa	2,8%	26,5 (0.1003)	216	69,6	No chunks in blender	Water looked clear
3	Suction	12 x 0.25" Medusa	2,7%	4,8 (0.0182)	39	62,4	No chunks in blender	Water looked clear
4	Suction	12 x 0.25" Medusa	2,8%	23,5 (0.0889)	192	70,1	No chunks in blender	Water looked clear
5	Suction	2" tee	2,9%	5,05 (0,0191)	43	64,2	No chunks in blender	Water looked clear
6	Suction	2" tee	3,0%	25 (0.0946)	219	70,0	No chunks in blender	No lumps on screen
7	Suction	2" tee	3,3%	25 (0.0946)	243	70,1	No chunks in blender	1 blob on screen
8	Suction	2" tee	3,3%	5,5 (0.0208)	54	69,7	Chunks floating in blender	No lumps on screen
C1	Tub	2" hose	2,9%	25 (0.0946)	212	67,9	Snake swirling in blender. Lots of 2" wide pieced hanging on edges of tank as it drained	3 blobs on screen (~0.5")

Table 1: Results of tests in the blender

gpm = gallons per minute, water flow rate 80 barrels per minute (12.7 m^3 / min)

Examples 1 to 4 demonstrate, that introducing the aqueous polymer concentrates through a plurality of inlets (“Medusa”) at the suction side yields good results. Using 1 single inlet (“tee”) also yields satisfying results, although at a concentration of 3.3 wt %, some chunks are observed.

Comparative example C1 clearly demonstrates that adding the aqueous polymer concentrate not at the suction side but through an opening directly into the blender tub does not yield a satisfying dissolution. In terms of friction reduction, the best performance measured on this instrument is typically 70-75%, depending on the conditions. All the measured values are close to this, and any deviations below this level are correlated to lower concentrations.

Claims

1. Process for making an aqueous treatment fluid comprising water-soluble polymers for treating subterranean formations by means of a device comprising at least

- a mixing vessel (1) comprising at least
  - an inlet (7) for an aqueous base fluid,
  - an inlet (3) for adding treatment fluid additives,
  - means (2) for mixing the contents of the mixing vessel, and
  - an outlet (8) for the aqueous treatment fluid,
- at least one source (4) for the aqueous base fluid,
- a suction pump (6), whose inlet side is connected with the source(s) (4) for the aqueous fluid by at least one first input tube (5), and whose pressure side is connected with the inlet (7) of the aqueous mixing vessel (1) by at least one second input tube (5'),
- a discharge pump (10), whose inlet side is connected with the outlet (8) by a discharge tube (9) and whose pressure side is connected with a product tube (11) which transfers the aqueous treatment fluid to a device for further handling or use,

wherein the device additionally comprises at least one inlet (12) for an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate, which is arranged at least

- at one of the first input tube(s) (5), and/or
- at one of the second input tube(s) (5'),

and wherein the process comprises at least the following steps:

(I) Continuously pumping a stream of an aqueous base fluid from the source(s) (4) through the input tube(s) (5) by means of the suction pump (6),

(II) continuously adding a stream of the aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate through the at least one inlet (11) to the stream of aqueous base fluid into

- at least one of the first input tube(s) (5), and/or
- at least one of the second input tube(s) (5'),

thereby obtaining a stream of a mixture of the aqueous base fluid and the aqueous polymer concentrate,

(III) introducing the obtained mixture into the mixing vessel (1) through the inlet (7), and mixing the components by means of the mixing means (2), thereby obtaining an aqueous treatment fluid,

(IV) continuously removing a stream of the aqueous treatment fluid from the mixing vessel (1) by means of the discharge pump (10) through the outlet (8) and the discharge tube (9) and transferring it into the product tube (11).

2. Process according to claim 1, wherein the aqueous polymer concentrate comprises 2.5 to 10 wt. % of the water-soluble polymer, relating to the total of all components of the polymer concentrate.

3. Process according to claims 1 or 2, wherein the aqueous polymer concentrate is an aqueous polyacrylamide concentrate.

4. Process according to any of claims 1 to 3, wherein the aqueous polymer concentrate is added into at least one of the first input tube(s) (5) or at least one of the second input tube(s) (5’) through one single inlet (12).

5. Process according to any of claims 1 to 3, wherein the aqueous polymer concentrate is added into at least one of the first input tube(s) (5) and/or at least one of the second input tubes (5’) through a plurality of inlets (12).

6. Process according to claim 5, wherein the number of inlets (12) is from 5 to 100 per tube.

7. Process according to any of claims 1 to 3, wherein the inlet (12) is connected with a distributor (15) which is a hollow body comprising a plurality of perforations, which is arranged in at least one of the first input tube(s) (5) and/or in at least one of the second input tube(s) (5’) and the stream of the aqueous base fluid circulates around the distributor, wherein the aqueous polymer concentrate is introduced through the inlet (12) into the distributor and pressed through its perforations.

8. Process according to any of claims 1 to 7, wherein the inlet(s) (12) are arranged at at least one of the first input tube(s) (5).

9. Process according to any of claims 1 to 7, wherein the inlet(s) (12) are arranged at at least one of the second input tube(s) (5’).

10. Process according to any of claims 1 to 9, wherein the source(s) (4) for the aqueous base fluid are tanks.

11. Process according to any of claims 1 to 10, wherein the device comprises a plurality of input tubes (5).

12. Process according to any of claims 1 to 11, wherein the means (2) for mixing the contents of the mixing vessel comprise at least one stirrer.

13. Process according to any of claims 1 to 12, wherein the process comprises adding at least a proppant through the inlet (3) into the mixing vessel.

14. Process according to any of claims 1 to 13, wherein the aqueous polymer concentrate has a viscosity of at least 1,000 mPas*s, measured at 10 s^{-1}.

15. Process for treating subterranean formations penetrated by at least a wellbore by preparing an aqueous treatment fluid comprising water-soluble polymers and injecting it into the wellbore, wherein the aqueous treatment fluid is prepared by a process according to any of claim 1 to 14.

16. Process according to claim 15, wherein the process is a process of fracturing subterranean formations, and the aqueous treatment fluid is injected into the wellbore at a rate and pressure sufficient to penetrate into the formation, and to initiate or extend fractures in the formation, wherein at least a part of the aqueous treatment fluid injected additionally comprises a proppant.

17. Device for making aqueous treatment fluids comprising water-soluble polymers comprising at least

    - a mixing vessel (1) comprising at least
        - an inlet (7) for an aqueous base fluid,
        - an inlet (3) for adding treatment fluid additives,
        - means (2) for mixing the contents of the mixing vessel, and
        - an outlet (8) for the aqueous treatment fluid,
    - at least one source (4) for the aqueous base fluid,
    - a suction pump (6), whose inlet side is connected with the source(s) (4) for the aqueous fluid by at least one first input tube (5), and whose pressure side is connected with the inlet (7) of the aqueous mixing vessel (1) by at least one second input tube (5’),
    - a discharge pump (10), whose inlet side is connected with the outlet (8) by a discharge tube (9) and whose pressure side is connected with a product tube (11) which transfers the aqueous treatment fluid to a device for further handling or use,

wherein the device additionally comprises at least one inlet (12) for an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate, which is arranged at least

- at one of the first input tube(s) (5), and/or
- at one of the second input tube(s) (5’).

18. Device according to claim 17, wherein the aqueous polymer concentrate comprises 2.5 to 10 wt. % of the water-soluble polymer, relating to the total of all components of the polymer concentrate.

19. Device according to claims 17 or 18, wherein the aqueous polymer concentrate is an aqueous polyacrylamide concentrate.

20. Device according to any of claims 17 to 19, wherein the aqueous polymer concentrate is added into at least one of the first input tube(s) (5) or at least one of the second input tube(s) (5’) through one single inlet (12).

21. Device according to any of claims 17 to 19, wherein the aqueous polymer concentrate is added into at least one of the first input tube(s) (5) and/or at least one of the second input tubes (5’) through a plurality of inlets (12).

22. Device according to claim 21, wherein the number of inlets (12) is from 5 to 100 per tube.

23. Device according to any of claims 17 to 19, wherein the inlet (12) is connected with a distributor (15) which is a hollow body comprising a plurality of perforations, which is arranged in at least one of the first input tube(s) (5) and/or in at least one of the second input tube(s) (5’) and the stream of the aqueous base fluid circulates around the distributor, wherein the aqueous polymer concentrate is introduced through the inlet (12) into the distributor and pressed through its perforations.

24. Device according to any of claims 17 to 23, wherein the inlet(s) (12) are arranged at at least one of the first input tube(s) (5).

25. Device according to any of claims 17 to 23, wherein the inlet(s) (12) are arranged at at least one of the second input tube(s) (5’).

26. Device according to any of claims 17 to 25, wherein the source(s) (4) for the aqueous base fluid are tanks.

27. Device according to any of claims 17 to 25, wherein the device comprises a plurality of input tubes (5).

28. Device according to any of claims 17 to 27, wherein the means (2) for mixing the contents of the mixing vessel comprise at least one stirrer.

29. Device for adding an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer into a stream of an aqueous fluid in a tube, wherein the tube comprises a plurality of inlets (12) for the aqueous polymer concentrate.

30. Device according to claim 29, wherein the number of inlets (12) is from 5 to 100 per tube.

31. Device for adding an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer into a stream of an aqueous fluid in a tube, wherein the tube comprises at least one inlet (12) for the aqueous polymer concentrate which is connected with a distributor (13) which is a hollow body comprising a plurality of perforations, which is arranged in the input tube (5) and the stream of the aqueous fluid circulates around the distributor.

32. Process for making an aqueous treatment fluid comprising water-soluble polymers for treating subterranean formations by means of a device comprising at least

- a mixing vessel (1) comprising at least
    - an inlet (7) for an aqueous base fluid,
    - an inlet (3) for adding treatment fluid additives,
    - means (2) for mixing the contents of the mixing vessel, and
    - an outlet (8) for the aqueous treatment fluid,
- at least one source (4) for the aqueous base fluid,
- a suction pump (6), whose inlet side is connected with the source(s) (4) for the aqueous fluid by at least one input tube (5), and whose pressure side is connected with the inlet (7),
- a discharge pump (10), whose inlet side is connected with the outlet (8) by a discharge tube (9) and whose pressure side is connected with a product tube (11) which transfers the aqueous treatment fluid to a device for further handling or use,

wherein the discharge tube (9) connecting the outlet (8) with the discharge pump (10) additionally comprises at least one inlet (12) for an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate, and wherein the process comprises at least the following steps:

(Ia) Continuously pumping a stream of aqueous base fluid by means of the suction pump (6) from the storing tank (4) through the input tube(s) (5) and the inlet (7) into the mixing vessel (1),

(IIa) adding treatment fluid additives through the inlet (3) and mixing the components in the mixing vessel (1) by means of the mixing means (2), thereby obtaining an aqueous treatment fluid,

(IIIa) continuously removing a stream of the aqueous treatment fluid from the mixing vessel (1) through the outlet (8) into the discharge tube (9) by means of the discharge pump (10),

(IVa) continuously adding a stream of the aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate through the inlet (12) to the stream of aqueous treatment fluid in the discharge tube (9), and

(Va) transferring the aqueous treatment fluid comprising the aqueous polymer concentrate through the discharge pump (10) into the product tube (11), thereby obtaining an aqueous treatment fluid comprising water-soluble polymers.

33. Device for making an aqueous treatment fluid comprising water-soluble polymers for treating subterranean formations by means of a device comprising at least

- a mixing vessel (1) comprising at least
    - an inlet (7) for an aqueous base fluid,
    - an inlet (3) for adding treatment fluid additives,
    - means (2) for mixing the contents of the mixing vessel, and
    - an outlet (8) for the aqueous treatment fluid,
- at least one source (4) for the aqueous base fluid,
- a suction pump (6), whose inlet side is connected with the source(s) (4) for the aqueous fluid by at least one input tube (5), and whose pressure side is connected with the inlet (7),
- a discharge pump (10), whose inlet side is connected with the outlet (8) by a discharge tube (9) and whose pressure side is connected with a product tube (11) which transfers the aqueous treatment fluid to a device for further handling or use,

wherein the discharge tube (9) connecting the outlet (8) with the discharge pump (10) additionally comprises at least one inlet (12) for an aqueous polymer concentrate comprising 1.0 to 10 wt. % of a water-soluble polymer, relating to the total of all components of the polymer concentrate.

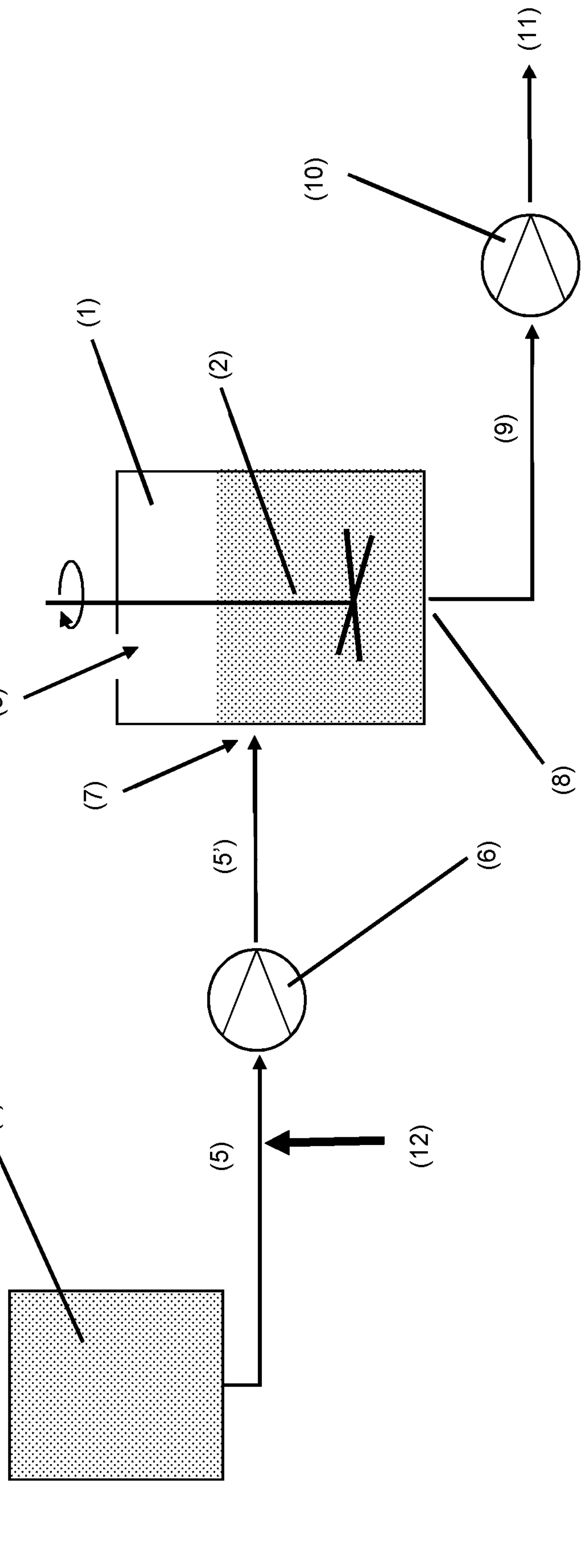

Figure 1

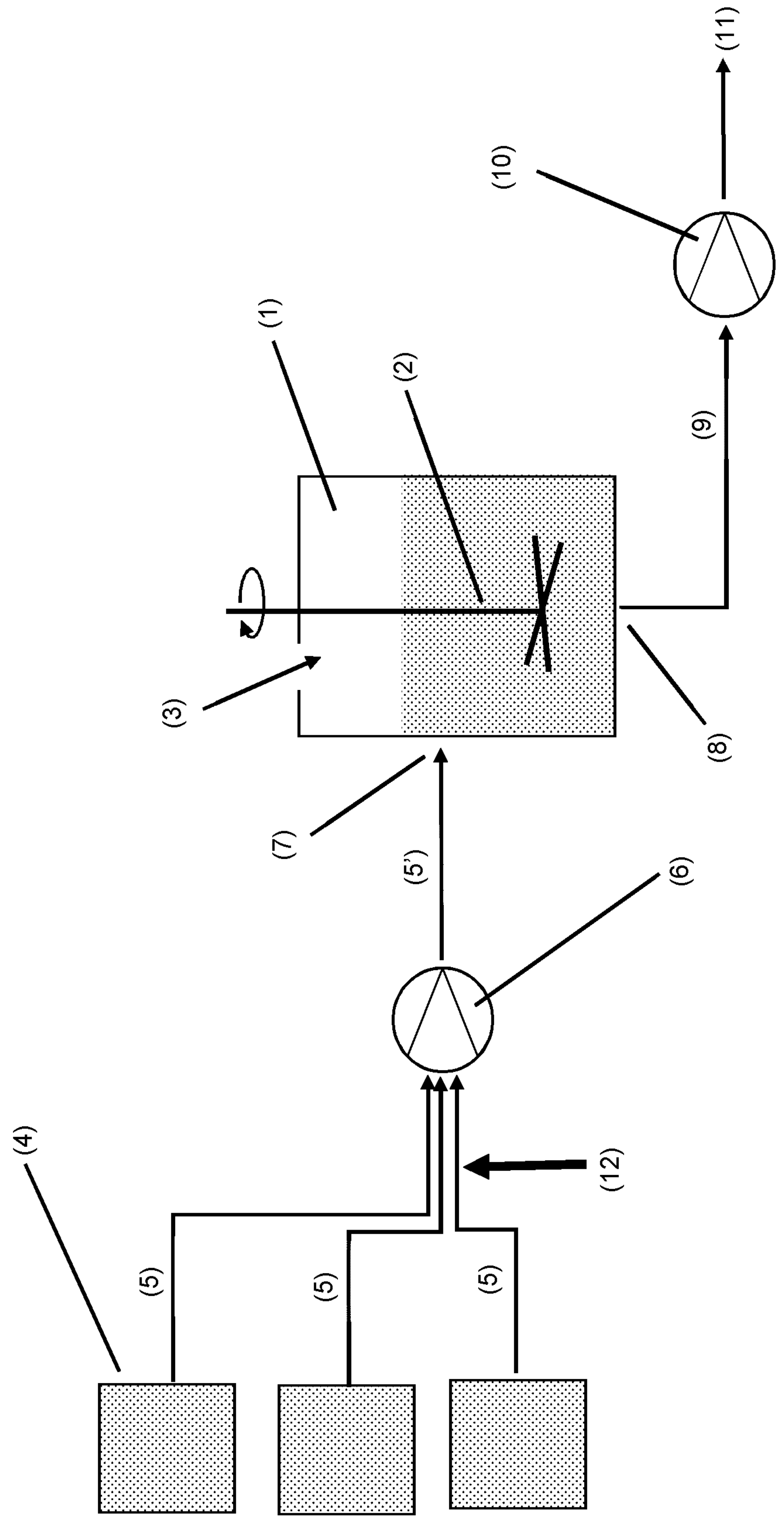

Figure 2

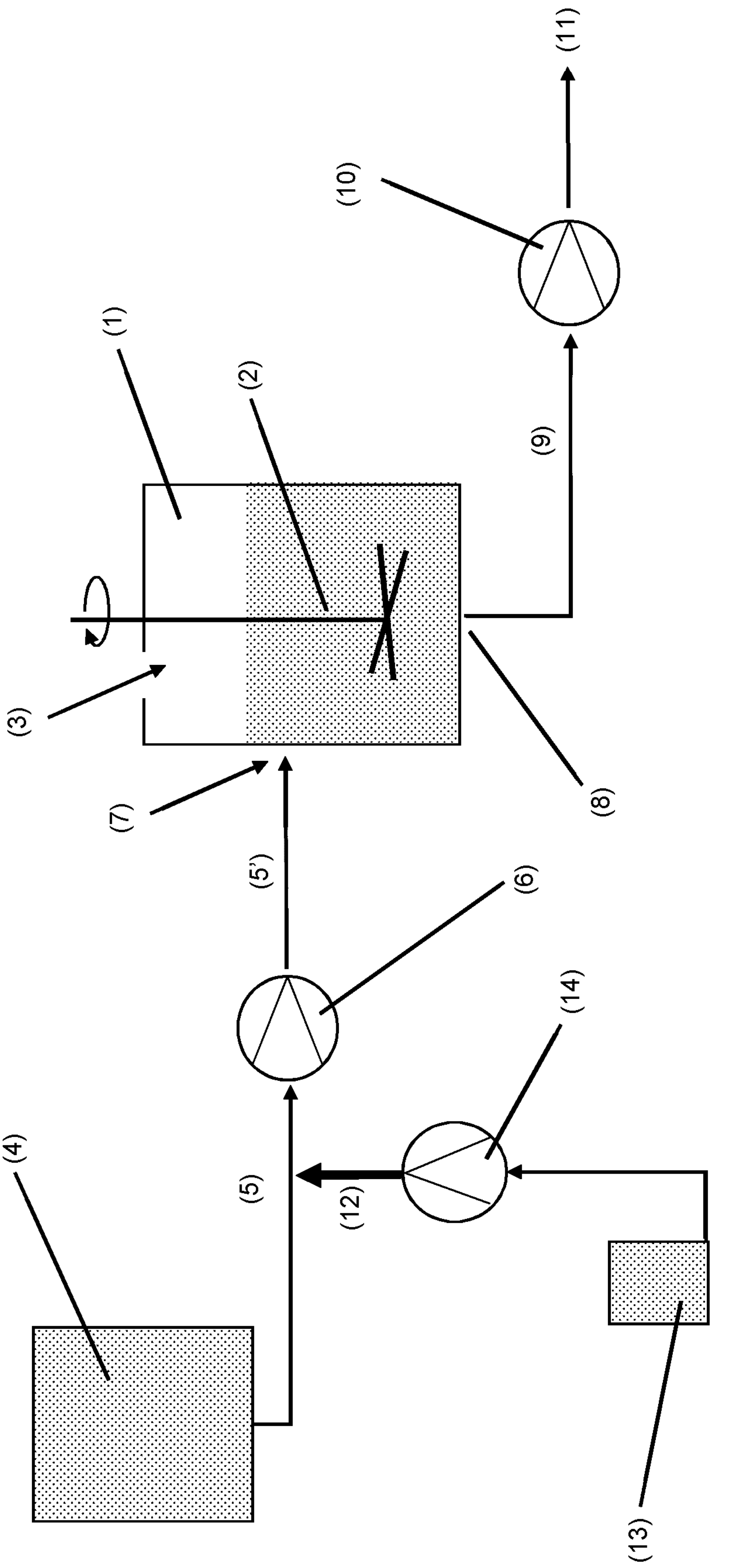

Figure 3

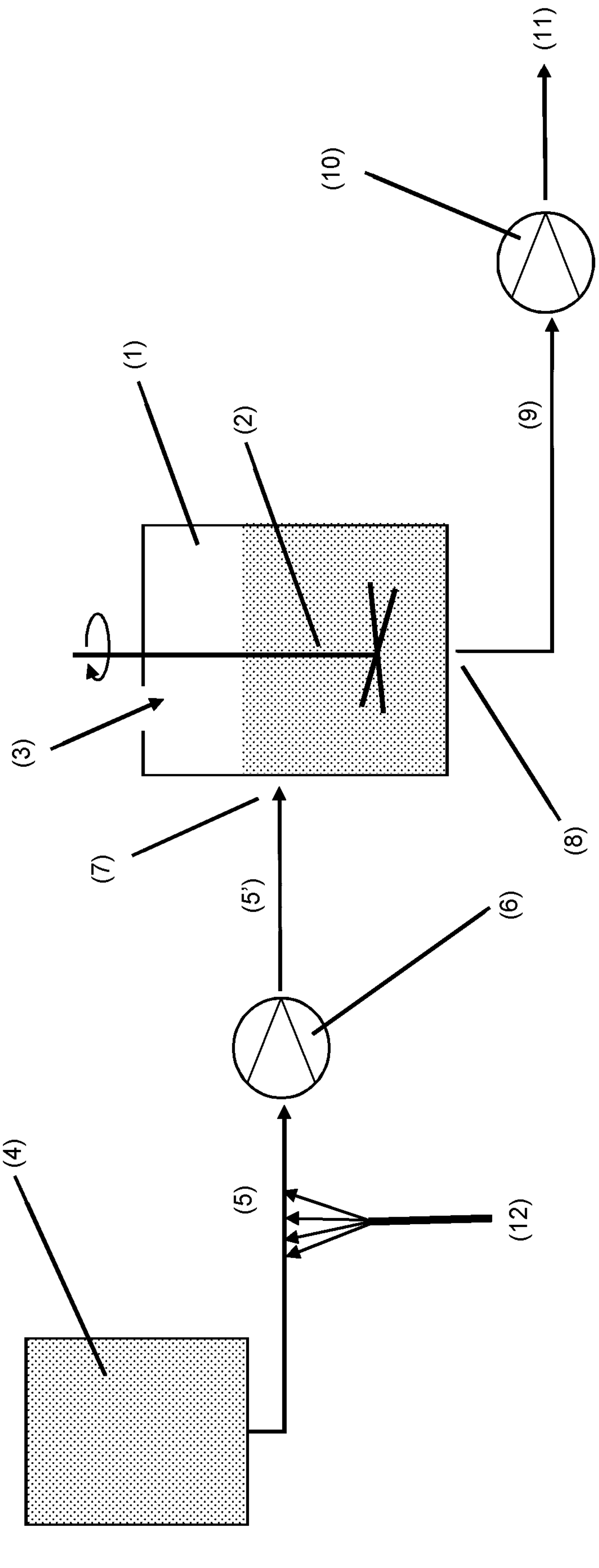

Figure 4

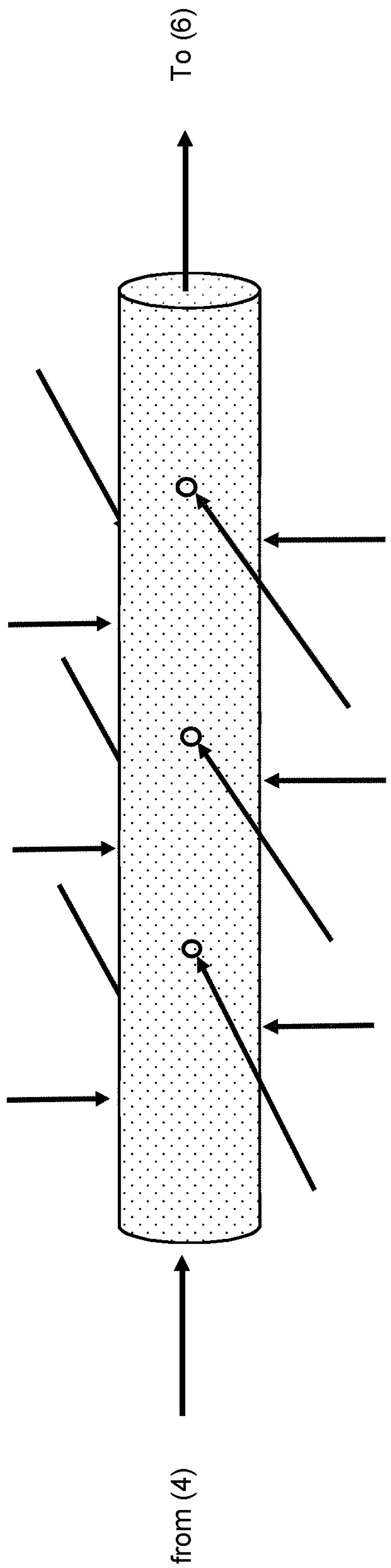

Figure 5

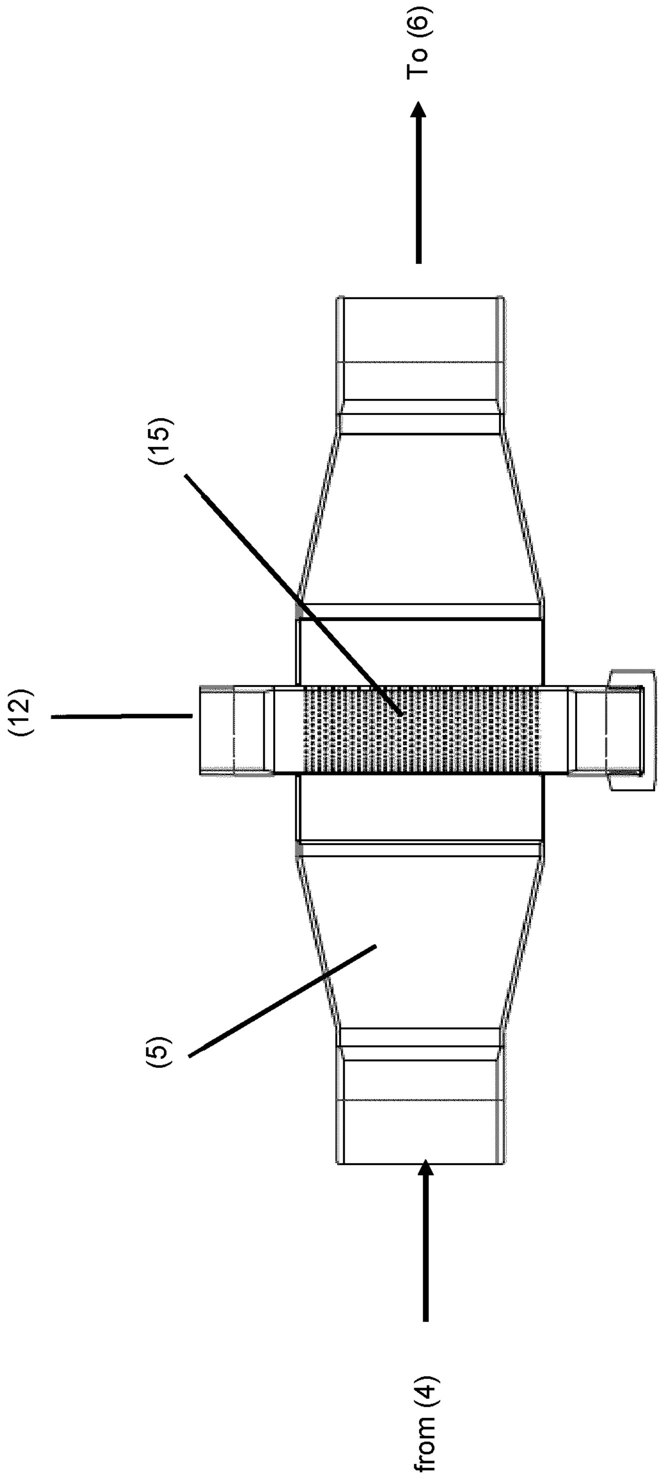

Figure 6

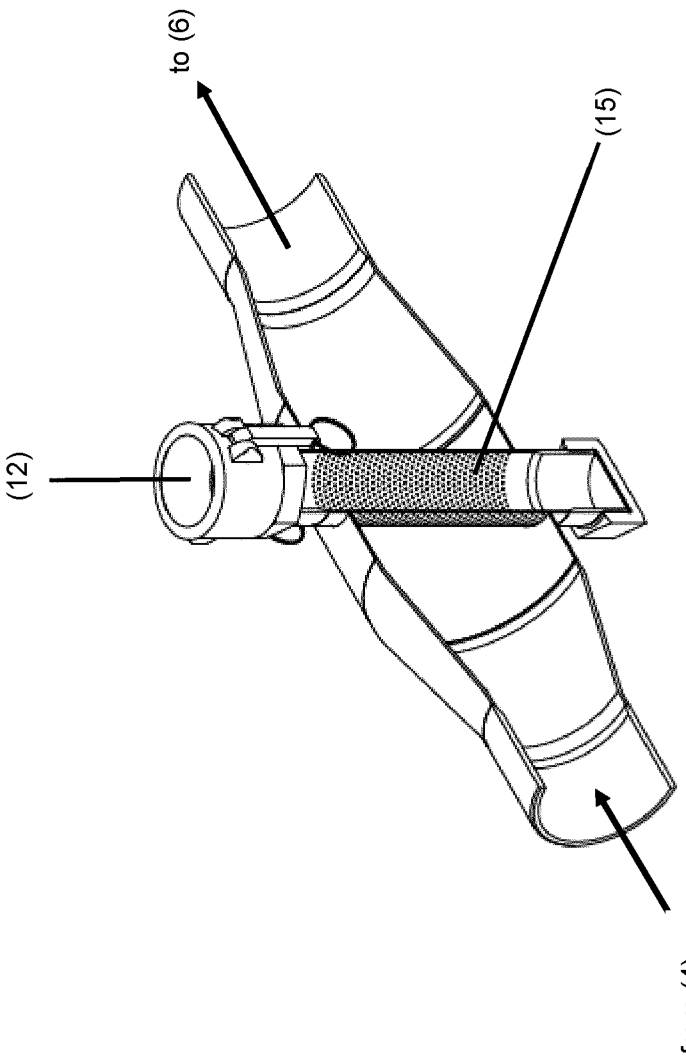

Figure 7

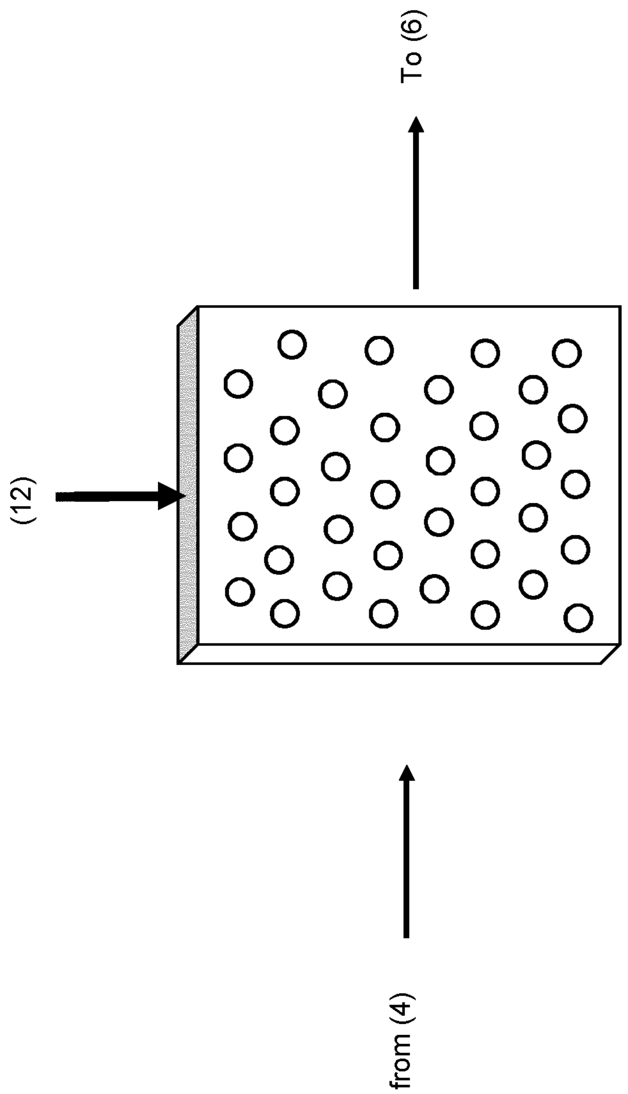

Figure 8:

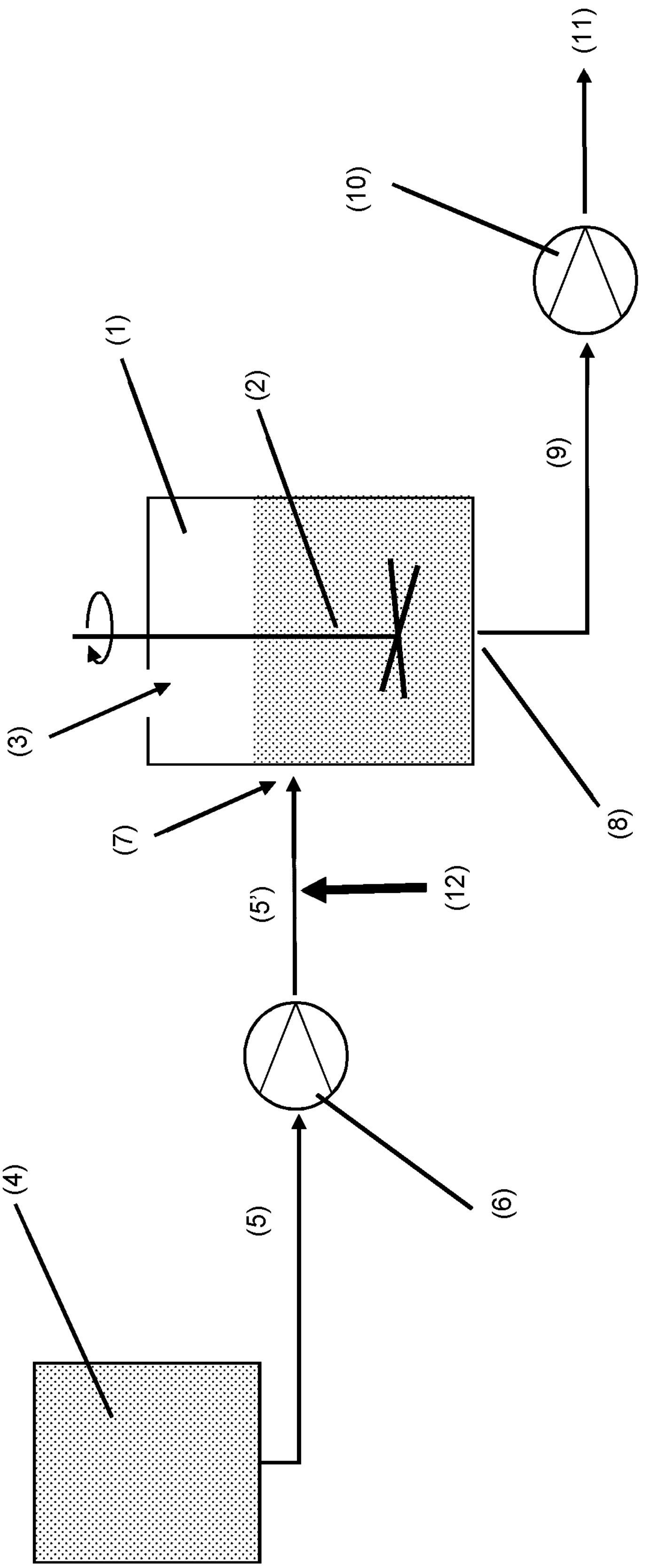

Figure 9:

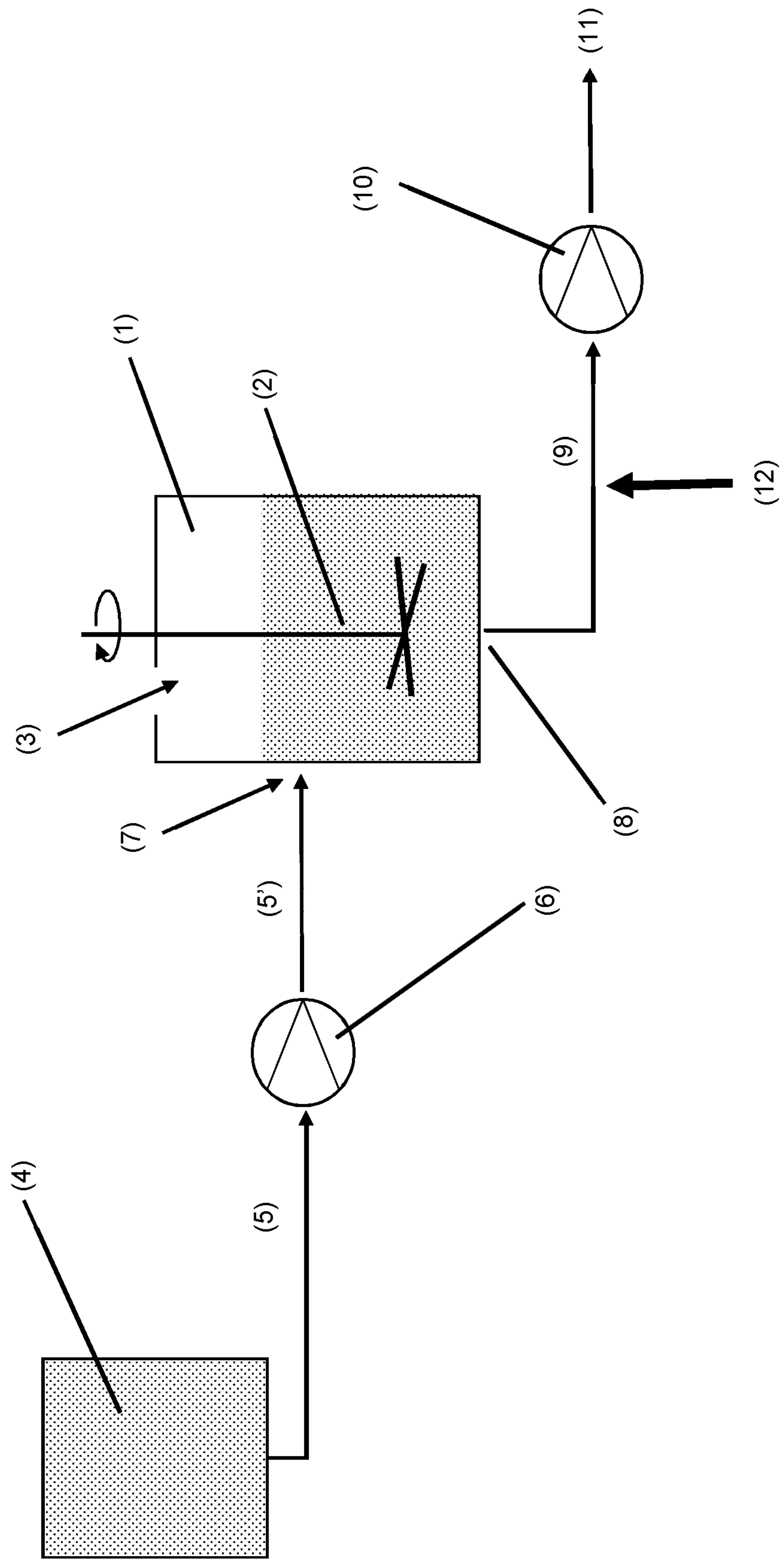

Figure 10:

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/060841

A. CLASSIFICATION OF SUBJECT MATTER
INV. E21B21/06 E21B43/16 E21B43/25 E21B43/26 B01F3/00 C09K8/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
E21B B01F C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 3 063 230 A1 (SNF SAS [FR]) 31 August 2018 (2018-08-31) cited in the application	1-6, 8-22, 24-28
Y	pages 1-2; figures 1-3	7,23,32, 33
Y	US 2003/196809 A1 (WILLBERG DEAN [US] ET AL) 23 October 2003 (2003-10-23) paragraphs [0029] - [0034]; figure 1	32,33
X	US 2015/133348 A1 (OLDHAM DON [US]) 14 May 2015 (2015-05-14) figures 1-7	29,30
X	US 5 392 855 A (BERNARDI JR LOUIS A [US] ET AL) 28 February 1995 (1995-02-28)	31
Y	column 1, line 61 - column 5, line 4	7,23

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 December 2020	12/01/2021

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/060841

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012/273206 A1 (ZAMORA FRANK [US] ET AL) 1 November 2012 (2012-11-01) paragraphs [0047] - [0080]; figures 1-2 -----	1-33

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2020/060841

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2012273206 A1	01-11-2012	NONE	