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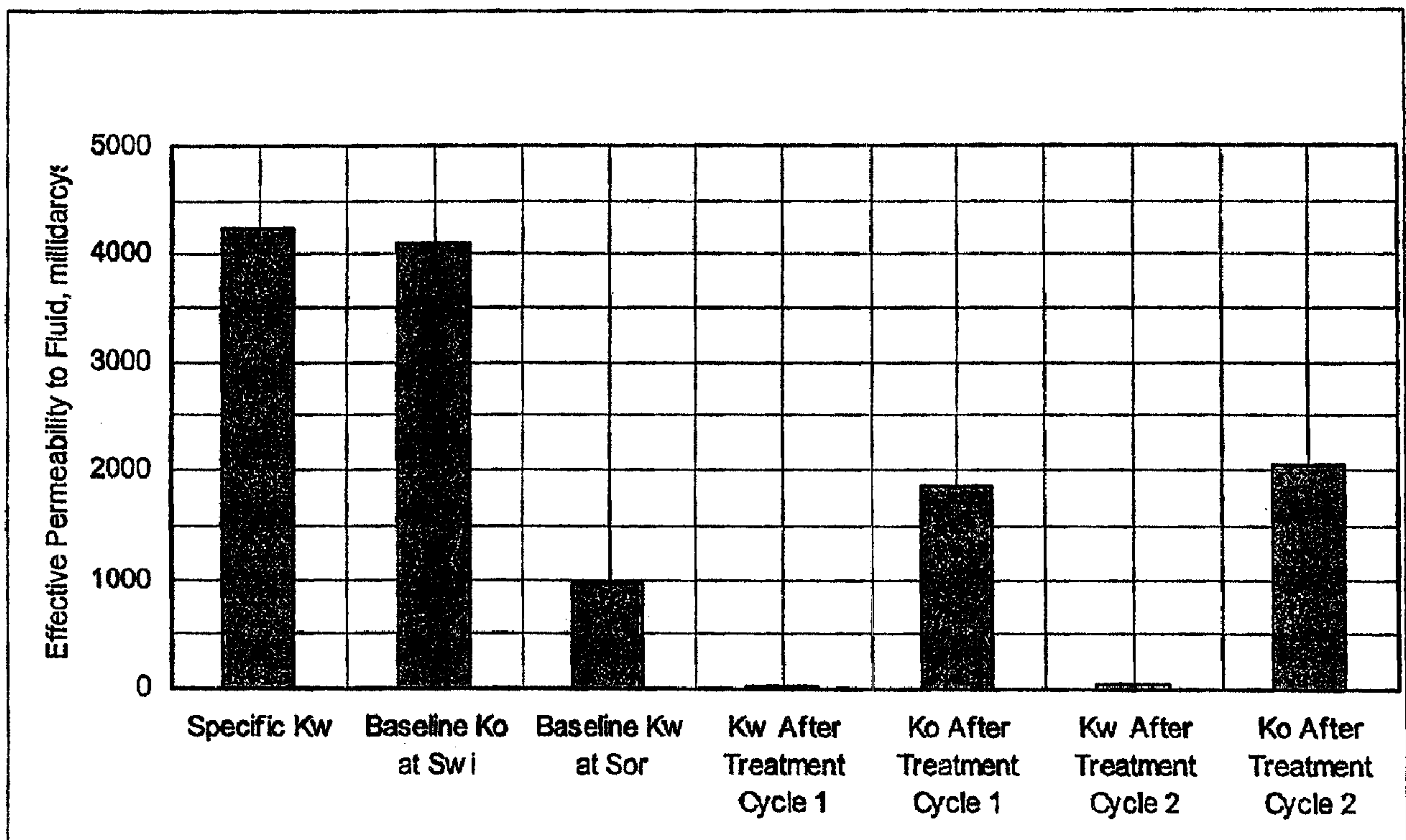
(72) Inventeurs/Inventors:
KALFAYAN, LEONARD J., US;
DAWSON, JEFFREY C., US

(73) Propriétaire/Owner:
BJ SERVICES COMPANY, US

(74) Agent: BERESKIN & PARR LLP/S.E.N.C.R.L.,S.R.L.

(54) Titre : COMPOSITIONS RENFERMANT DES COMPOSES ORGANOSILICIÉS POUR AMÉLIORER LA
PRODUCTION D'HYDROCARBURES ET MÉTHODE POUR LES UTILISER

(54) Title: ORGANOSILICON CONTAINING COMPOSITIONS FOR ENHANCING HYDROCARBON PRODUCTION AND
METHOD OF USING THE SAME



(57) Abrégé/Abstract:

Compositions useful in the reduction of excessive water in oil and gas wells and other subterranean formations comprises an organosilicon compound and a relative permeability modifier (RPM) macromolecule. The RPM is capable of impeding the production of water. The organosilicon compound is capable of forming a water-soluble silanol by hydrolysis and is preferably

(57) Abrégé(suite)/Abstract(continued):

either an organosilane halide or organosilane alkoxide. The composition is introduced into the subterranean formation for the purpose of selectively reducing excessive production of aqueous fluids. The composition may be employed in well treatment fluids introduced into production wells or injection wells. The compositions may also be utilized in conjunction with stimulation treatments and with introduction of other well treatment fluids. By introducing the composition into fluid passages of the formation, the water producing zones can be selectively blocked off. Thus, the ability of fluids to flow through the aqueous fluid containing fluid passages is selectively reduced resulting in the reduced production of aqueous fluids while maintaining production of hydrocarbons. Core flow test results show effectiveness at permeability as high as 7.0 Darcy under high rate flow conditions.

ABSTRACT OF THE DISCLOSURE

Compositions useful in the reduction of excessive water in oil and gas wells and other subterranean formations comprises an organosilicon compound and a relative permeability modifier (RPM) macromolecule. The RPM is capable of impeding the production of water. The organosilicon compound is capable of forming a water-soluble silanol by hydrolysis and is preferably either an organosilane halide or organosilane alkoxide. The composition is introduced into the subterranean formation for the purpose of selectively reducing excessive production of aqueous fluids. The composition may be employed in well treatment fluids introduced into production wells or injection wells. The compositions may also be utilized in conjunction with stimulation treatments and with introduction of other well treatment fluids. By introducing the composition into fluid passages of the formation, the water producing zones can be selectively blocked off. Thus, the ability of fluids to flow through the aqueous fluid containing fluid passages is selectively reduced resulting in the reduced production of aqueous fluids while maintaining production of hydrocarbons. Core flow test results show effectiveness at permeability as high as 7.0 Darcy under high rate flow conditions.

**Title: ORGANOSILICON CONTAINING COMPOSITIONS FOR
ENHANCING HYDROCARBON PRODUCTION AND METHOD OF USING
THE SAME**

Field of the invention

5 This invention relates generally to methods and compositions for modifying the permeability of subterranean formations. In particular, this invention relates to methods and compositions for selectively reducing the production of water from subterranean formations; the composition being a water control treatment fluid containing a relative permeability modifier (RPM)
10 macromolecule and an organosilicon compound.

Background of the invention

Production of water and aqueous fluids from oil and gas wells is a common phenomenon which poses a variety of problems. For example, water
15 production typically reduces the amount of oil and/or gas that may be ultimately recovered from a well since the water takes the place of other fluids that may flow or be lifted from the well. Thus, water production from oil and gas wells causes significant economic drawbacks. High water rates cause a reduction in well productivity and increase in operating expenditures.
20 Furthermore, operating costs associated with disposal of produced water in an environmentally safe manner typically increase with the volume of produced water, thus increasing the threshold amount of hydrocarbons that must be produced in order to continue economical production of the well.

U.S. Patent No. 6,228,812 discloses a chemical treatment that selectively
25 reduces water production. Such treatments employ relative permeability modifiers (RPMs). The use of RPMs offer several advantages. For instance, the use of RPMs reduces costs since the chemicals are used in limited quantities and the treatment does not require zonal isolation. In addition, the use of RPMs entails low risk since the polymer reduces the water permeability
30 without affecting oil permeability. Further, RPMs are simple to apply and do not require expensive equipment, such as rigs, for their application.

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However, even the most superior RPMs are not certain to impart long-lasting effectiveness, nor exhibit a high degree of water flow resistance relative to oil flow, especially when formation permeability rises above 1 Darcy. New RPM systems are needed for higher permeability applications.

5 Summary of the invention

Compositions useful for selective permeability modification of subterranean formations to reduce or substantially eliminate the amount of water produced from oil and/or gas wells comprise a relative permeability modifier (RPM) macromolecule capable of impeding the production of water
 10 and an organosilicon compound. The compositions of the invention reduce or eliminate the production of water in an oil or gas well without substantially affecting the production of hydrocarbons.

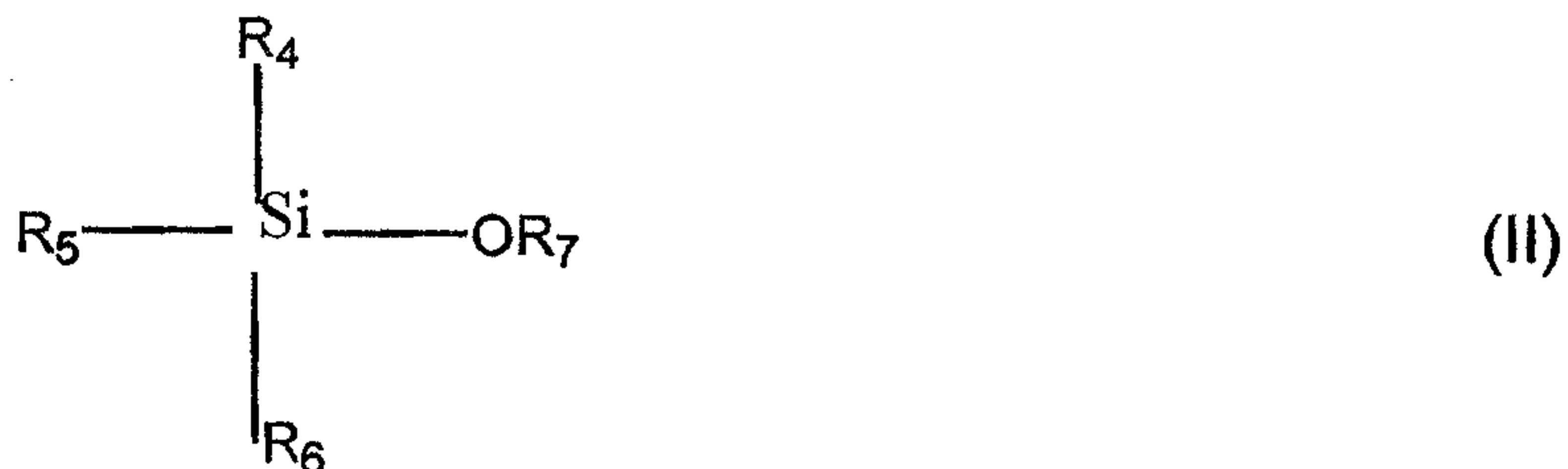
Suitable as the RPM are homopolymers and copolymers of acrylamide, optionally having been sulfonated or quaternized, polyvinylalcohol,
 15 polysiloxane, or a hydrophilic polymer selected from natural gums and chemically modified derivatives thereof.

In a preferred embodiment, the organosilicon compound is of the formula:



wherein R is a halogen, hydrogen, or an amine radical which can be
 20 substituted with hydrogen, organic radicals, or silyl groups, R₁ is hydrogen, an amine, or an organic radical having from 1 to 50 carbon atoms, and R₂ and R₃ are hydrogen or the same or different halogens, alkyl, alkenyl, aryl or amines having 1 to 50 carbon atoms; or

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wherein R_4 , R_5 and R_6 are independently selected from hydrogen, amine, halogen, alkoxide, and organic radicals having from 1 to 50 carbon atoms, provided not all of R_4 , R_5 and R_6 are hydrogen, and R_7 is an organic radical having from 1 to 50 carbon atoms.

5 The organosilicon compound increases flow resistance and is believed to attach to the RPM polymer as well as to the mineral surfaces of the formation. As a result, the effective RPM permeability application range is significantly extended with the novel compositions.

10 The compositions of the invention are designed to partition both onto reservoir rock and into reservoir brines. Such behavior results in significant reduction of permeability in water-rich environments.

Advantageously, the disclosed method and compositions are relatively non-damaging to oil permeability, for example, in oil saturated sandstone while exhibiting the ability to decrease water permeability substantially in
15 water saturated zones. Therefore, the disclosed compositions may be applied successfully to a productive zone without the necessity of mechanical isolation in the wellbore. It will be understood with benefit of this disclosure that mechanical isolation, such as isolation of a water producing section or perforations, may be employed if so desired, however, such measures may
20 add significant costs to a water control treatment. Consequently, treatments utilizing the disclosed method and compositions without mechanical isolation are considerably less expensive than conventional methods which require such measures.

In one respect, disclosed is a method for treating a subterranean
25 formation, including introducing an aqueous composition into the formation wherein the concentration of RPM in the aqueous composition is between from about 100 to about 80,000 ppm, preferably from about 500 to about

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10,000 ppm, and the concentration of organosilicon compound is between from about 500 to about 20,000 ppm. While not intending to be bound to any theory, it is believed that the organosilicon compound is capable of binding both to the RPM as well as formation substrate minerals in the well.

5 The invention has particular applicability in those situations where the formation permeability in the oil or gas well is between from about 0.1 to about 8,000 md. Further, the formation substrate minerals may include quartz, clay, shale, silt, chert, zeolite, or a combination thereof.

10 In the practice of this method, the composition is a water control treatment fluid which may optionally be a stimulation fluid. The water control treatment fluid may be introduced into the subterranean formation prior to, together with, or following a hydraulic fracturing or stimulation fluid treatment.

15 In one embodiment, the composition of the invention may be used to contact the subterranean formation and substantially reduce permeability to water within the formation without substantially reducing permeability to oil within the formation. In another embodiment, the composition of the invention may be used to contact the subterranean formation so that it has a post-treatment resistance factor, for water of greater than or equal to about 5 and a post-treatment resistance factor for oil of less than 2, as measured across a
20 Berea core, such as about 2.5 cm diameter by about 4 cm long and having a permeability to nitrogen of about 1000 md, each of the water and oil resistance factors being measured at stable laminar flow rate at constant pressure.

25 **Brief description of the drawings**

 In order to more fully understand the drawings referred to herein, a brief description of each drawing is presented, in which:

 FIG. 1 illustrates results obtained by use of a water treatment fluid containing 3% RPM and 0.5% of an aqueous solution containing
30 approximately 50% organosilicon compound in a high permeability Berea core. As used herein all percentages are weight percentages unless otherwise noted.

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FIG. 2 illustrates results obtained by use of a water treatment fluid containing 4% RPM and 0.3% of an aqueous solution containing approximately 50% organosilicon compound in a high permeability Berea core.

5 FIG. 3 illustrates results obtained by use of a water treatment fluid containing 5% RPM and 0.5% of an aqueous solution containing approximately 50% organosilicon compound in a high permeability Berea core.

Each of the figures demonstrates that treatment of an oil or gas well
10 with the aqueous system of the invention significantly reduces water flow relative to oil flow in very high permeability cores.

Detailed description of the invention

The aqueous compositions of the invention described herein may be
15 utilized in well treatment methods to selectively reduce the permeability of a subterranean formation to water, while at the same time leaving the permeability of the formation to oil virtually unchanged. In a preferred embodiment, the post-treatment resistance factor for water is greater than or equal to 5.0, preferably in excess of 9 or more. Furthermore, the disclosed
20 compositions, when introduced into a formation, tend to exhibit a high resistance to removal from water bearing areas of the formation over time.

The aqueous compositions of the invention contain a relative permeability modifier (RPM) and an organosilicon compound.

The RPM for use in the invention is any polymer that can impede the
25 production of water and which provides suitable attachment, such as grafting, sites for the organosilicon compound. Most often the RPM is hydrophilic having the ability to remain hydrated in the formation waters and simultaneously having an affinity to adsorb onto the solid formation material. Such RPMs typically have weight average molecular weights ranging from
30 about 50,000 to about 20,000,000 g/mole, preferably from about 100,000 to about 5,000,000 g/mole, most preferably from about 250,000 to about 2,000,000 g/mole.

In addition to the molecular weight, the RPMs must also have specific sites that allow interaction with the organosilicon compound. Most often, interaction of the RPM polymeric material and the silicon-containing organic compound occurs with any oxygen containing pendent group on the polymeric material, particularly the hydroxyl group. However, many of the silicon-based agents are multifunctional having additional functional groups attached to the silicon-based agent. In most cases, these additional groups are generally non-oxygen-bearing groups, but could also interact with specific sites on the RPM. The additional functional groups on the silicon-containing organic compound include amines, isocyanates, amides, thio-based and phosphorus-based groups. These additional functional groups can also interact with the specific sites of the RPM. For example, amine functional groups on the silicon-containing organic compound can interact with polymers having carboxylic acid groups or aldehyde groups to form either amides or Schiff bases. Another example is silicon-based agents having isocyanate or isothiocyanate functional groups that can interact with amine- or alcohol-based RPMs to produce urethane type linkages.

Any RPM that offers an attachment site for the organosilicon compound will provide, to some degree, a favorable response to impede water production and thus be sufficient as the RPM. Suitable RPMs include those referenced in U.S. Patent Nos. 5,735,349; 6,169,058; and 6,228,812.

Suitable RPMs include copolymers of hydrophilic monomers and a second monomer. Hydrophilic monomers may include both ionic and nonionic monomers. The term "nonionic monomer" refers to monomers that do not ionize in aqueous solution at neutral pH. In addition, an anionic monomer, such as salts of acrylates, may be used in conjunction with a cationic monomer. Examples of suitable nonionic hydrophilic monomers include, but are not limited to acrylamide, (meth)acrylamide, N-vinyl pyrrolidone, N-vinyl formamide and N-vinylacetamide. Ionic monomers may be either anionic or cationic. Examples of anionic monomers include, but are not limited to, alkaline salts of acrylic acid, ammonium or alkali salts of

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acrylamidomethylpropane sulfonic acid ("AMPS"), acrylic acid, (meth)acrylic acid, maleic acid, itaconic acid, styrene sulfonic acid, and vinyl sulfonic acid (or its ammonium or alkali metal salts). Examples of suitable cationic monomers include, but are not limited to, dimethyldiallyl ammonium chloride and quaternary ammonium salt derivatives from acrylamide or acrylic acid such as acrylamidoethyltrimethyl ammonium chloride. Suitable as the second monomer are N-vinylformamide, N-methylacetamide, N,N-diallylacetamide, methylenebisacrylamide or a mixture thereof.

Preferred polymers applicable for use in the invention as the RPM include homopolymers, copolymers and terpolymers based on acrylamide, particularly those that are sulfonated or quaternized for solubility in high saline formation brines. In a preferred mode, such acrylamide copolymers may contain other components such as acrylic acid or (meth)acrylic acid, or a salt thereof, dimethyldiallylammonium chloride, acrylamidoethyltrimethylammonium chloride, methacrylamidoethyltrimethylammonium chloride, acrylamidomethylpropanesulfonic acid (AMPS), N-vinyl pyrrolidone, N-vinyl formamide, N-vinyl acetamide, N-vinylmethylacetamide, acrylamidoethyltrimethylammonium chloride, vinyl sulfonic acid, maleic acid, itaconic acid, styrene sulfonic acid, vinylsulfonic acid, methylenebisacrylamide and vinylphosphonic acid and sulfonate monomers thereof.

RPMs may further include homopolymers or copolymers which include the following monomeric units: acrylic acid, (meth)acrylic acid, dimethyldiallylammonium chloride as well as acrylamidoethyltrimethylammonium chloride, methacrylamidoethyltrimethylammonium chloride, acrylamidomethylpropanesulfonic acid (AMPS), N-vinyl pyrrolidone, N-vinyl formamide, N-vinyl acetamide, N-vinylmethylacetamide, acrylamidoethyltrimethylammonium chloride, maleic acid, itaconic acid, styrene sulfonic acid, vinylsulfonic acid and vinylphosphonic acid and sulfonate monomers, i.e., those monomers containing SO_3 pendant or functional groups and salts thereof, such as those derived with sodium or potassium, or quaternary

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ammonium salts. The chloride counter ion referenced above may also be substituted, for example, with any other halogen, sulfate, or phosphate. Other suitable monomeric units include dimethyldiallyl ammonium sulfate, methacrylamido propyl trimethyl ammonium bromide, and methacrylamido
 5 propyl trimethyl ammonium bromide.

For example, in one embodiment of the invention, the RPM may include at least one nonionic vinylamide monomer of the formula:



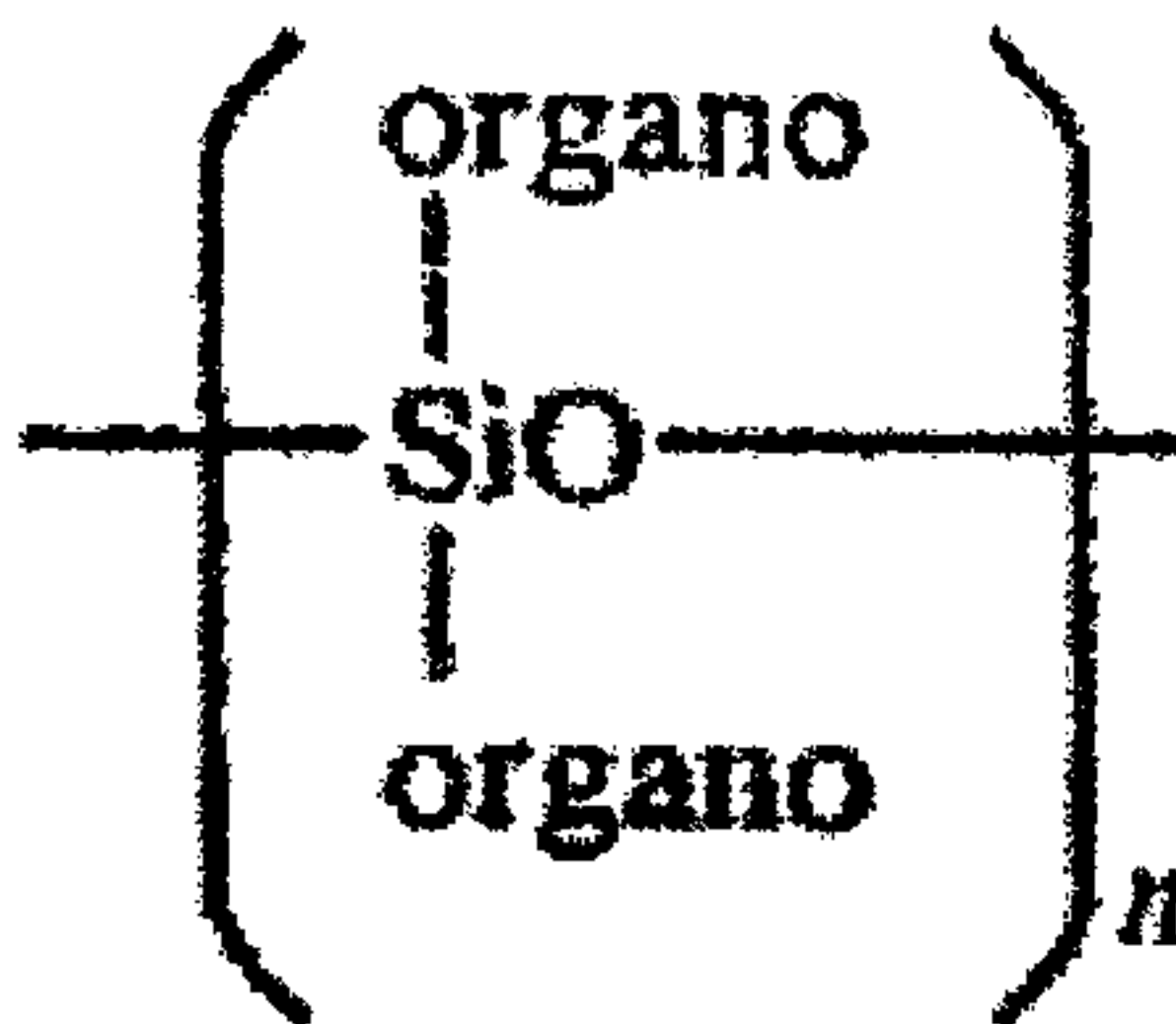
where R and R' independently represent a hydrogen, methyl, ethyl or propyl
 10 moiety. In a second embodiment, the RPM may further include at least one monomer containing anionic moieties of the formula:



where X represents a moiety containing a carboxylic acid or salt of that acid or a moiety containing a salt of a sulfonic acid or the salt of a sulfuric acid.

15 Lastly, synthetic polymers based on vinyl acetate to produce polyvinylalcohol (PVA) are also applicable as are polysiloxanes or silicones. The most preferred polymers are PVA having degrees of hydrolysis between from about 50% to about 100% and polyacrylamides as described in US patent 6,228,812 B1 and 5,379,841.

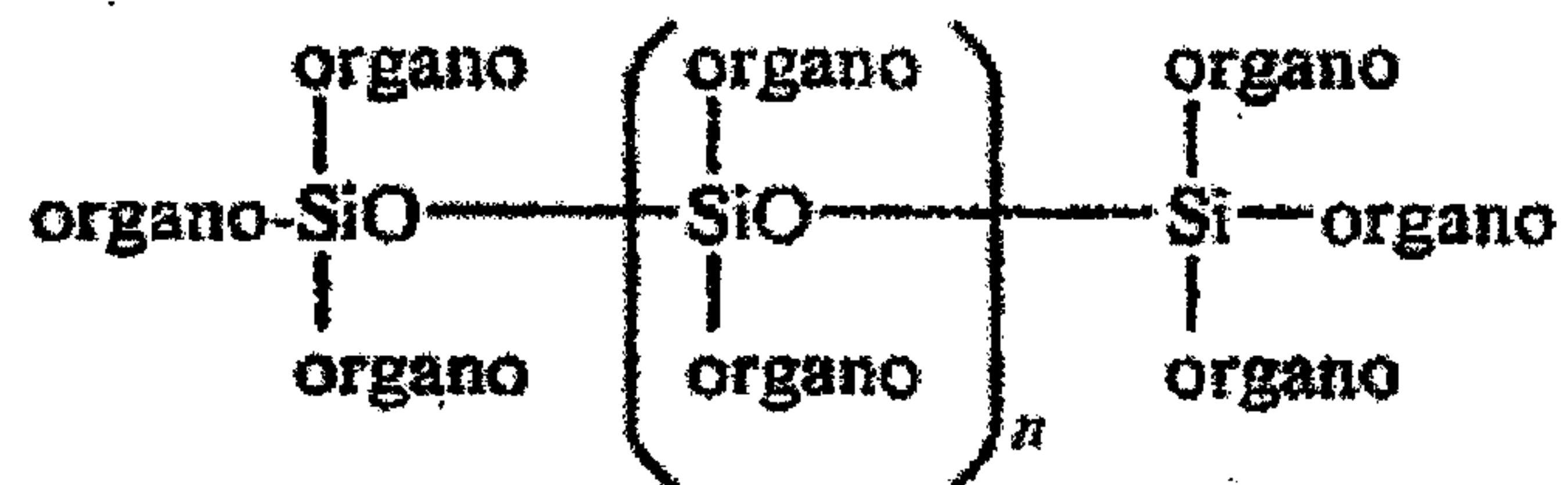
20 In general the silicones are polymers containing the following units:



of molecular weight sufficient to afford a viscosity suitable for use in well treatment methods known to those of skill in the art. Generally, the polysiloxanes for use as the RPM have a maximum molecular weight of about
 25 20,000 to about 30,000 or an n value from 2 to about 500, though higher molecular weights may be formed in situ.

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Preferred polysiloxanes include polysiloxane polyalkyl polyether copolymers. The preferred organo group is a mixture of hydrocarbon such as alkyl and alkoxide and most preferably being methyl and methoxide or ethoxide. Inclusive of preferred polysiloxanes are those of the formula:



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Suitable hydrophilic polymers further include natural gums such as guar, carrageenan, gum Arabic, gum ghatti, karaya, tragacanth, pectin, starch, locust bean gum, scleroglucan, tamarind and xanthan gums and any chemically modified derivatives of these gums including derivatives of cellulose such as the pendent derivatives hydroxyethyl, hydroxypropyl, hydroxypropylcarboxymethyl, hydroxyethylcarboxymethyl, carboxymethyl or methyl.

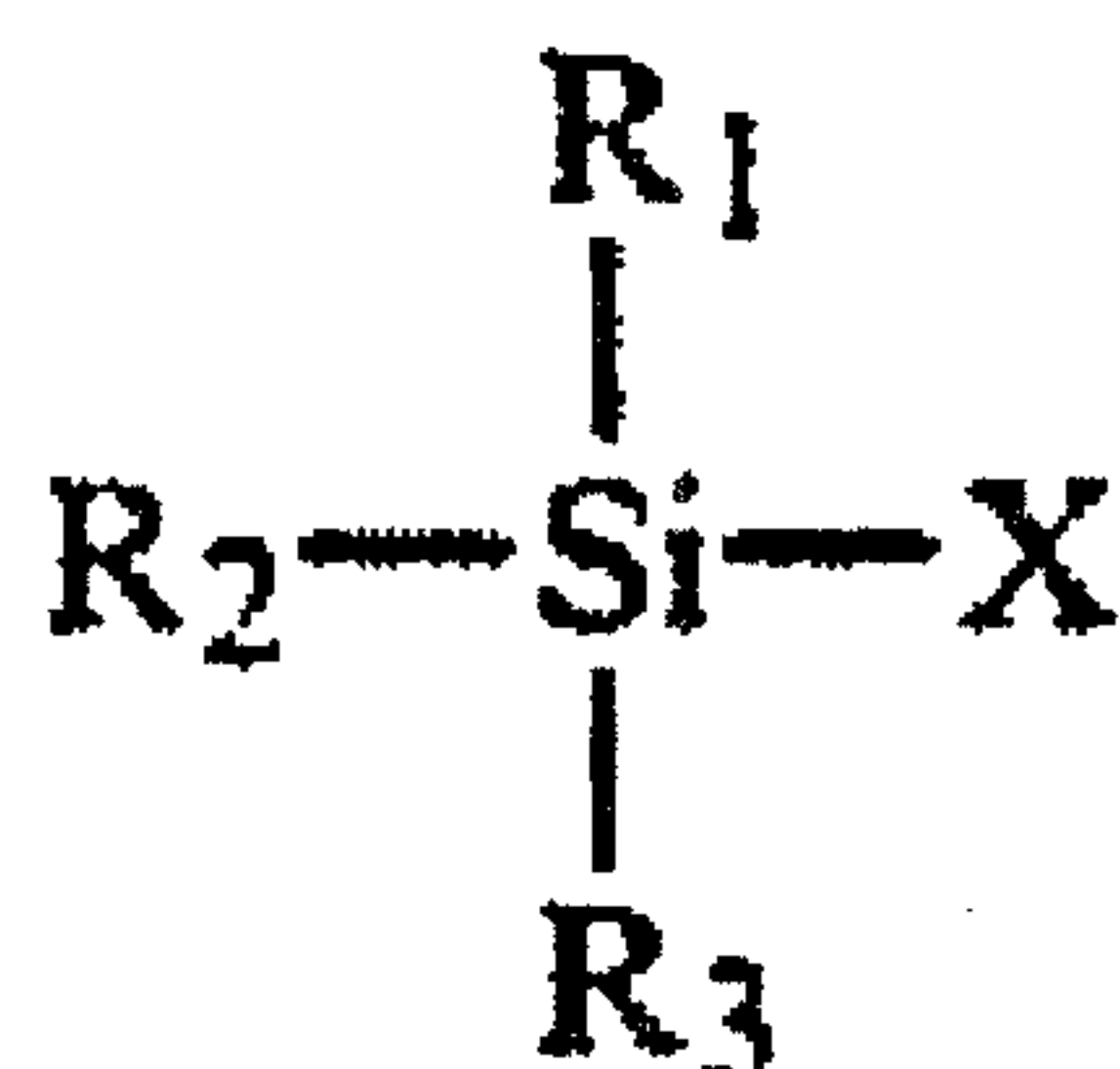
The organosilicon compounds for use in the aqueous compositions are generally capable of binding both to the RPM as well as to formation substrate minerals including quartz, clay, chert, shale, silt, zeolite or a combination thereof.

Suitable water-soluble organosilicon compounds for the invention include, without limitation, amino silanes such as 3-aminopropyltriethoxy silane and N-2-aminoethyl-3-aminopropyltrimethoxy silane, and vinyl silane compounds such as vinyl tris-(2-methoxyethoxy) silane. However, as discussed by M. R. Rosen, "From Treating Solution to Filler Surface and Beyond. The Life History of a Silane Coupling Agent," *Journal of Coatings Technology*, Vol. 50, No. 644, pages 70-82 (1978), many organosilane compounds are water-soluble for prolonged periods of time after they hydrolyze to form silanols, and temperatures can serve to aid the hydrolysis. For purposes of the present invention, then, compounds which form water-soluble silanols by hydrolysis will be considered as equivalent to the originally

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water-soluble organosilicon compounds. Such organosilicon compounds include organosilane halides and organosilane alkoxides.

Among the organosilanes especially suitable for use in this invention are those organosilane halides of the formula:

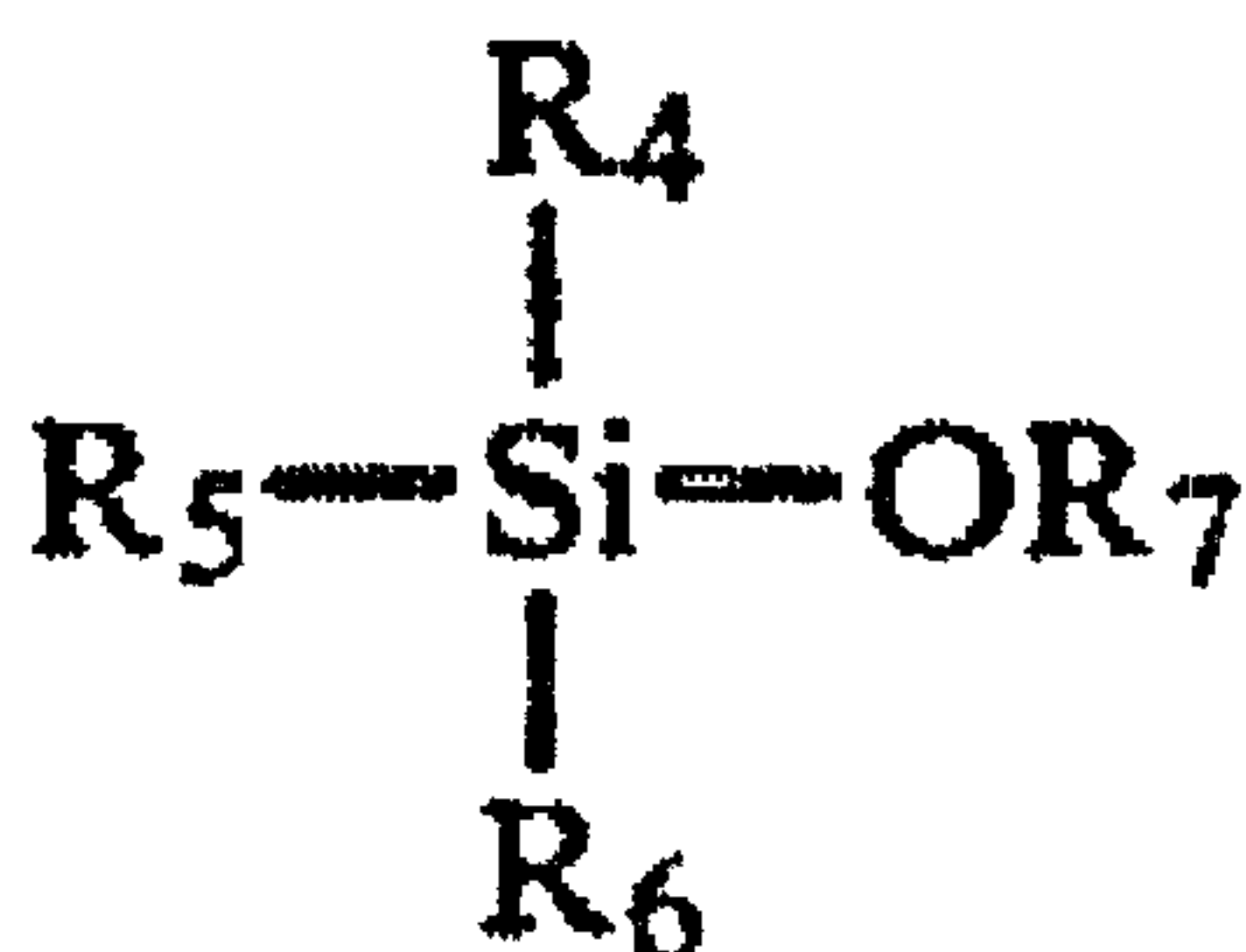


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wherein X is a halogen, R₁ is an organic radical having from 1 to 50 carbon atoms, and R₂ and R₃ are the same or different halogens as X or organic radicals of R₁. Preferably, X is a halogen selected from the group consisting of chlorine, bromine and iodine with chlorine being preferred, R₁ is an alkyl, alkenyl, alkoxide or aryl group having from 1 to 18 carbon atoms and R₂ and R₃ are the same or different halogens, or alkyl, alkenyl, alkoxide or aryl group having from 1 to 18 carbon atoms.

Suitable specific organosilane halides include methyldiethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, dimethyldibromosilane, diethyldiiodosilane, dipropyldichlorosilane, dipropyldibromosilane, butyltrichlorosilane, phenyltribromosilane, diphenyldichlorosilane, tolyltribromosilane, methylphenyldichlorosilane, propyldimethoxychlorosilane and the like.

Among the organosilane alkoxides suitable for use in this invention are those having the formula:



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wherein R_4 , R_5 , and R_6 are independently selected from hydrogen and organic radicals having from 1 to 50 carbon atoms, provided not all of R_4 , R_5 , and R_6 are hydrogen, and R_7 is an organic radical having from 1 to 50 carbon atoms. Preferably, R_4 , R_5 , and R_6 are independently selected from hydrogen, amine, alkyl, alkenyl, aryl, and carbhydryloxy groups having from 1 to 18 carbon atoms, with at least one of the R_4 , R_5 , and R_6 groups not being hydrogen, and R_7 is selected from amine, alkyl, alkenyl, and aryl groups having from 1 to 18 carbon atoms. When R_4 , R_5 , and R_6 are carbhydryloxy groups, alkoxy groups are preferred.

Suitable specific organosilane alkoxides include methyltriethoxysilane, dimethyldiethoxysilane, methyltrimethoxysilane, divinyl dimethoxysilane, divinyl di-2-methoxyethoxy silane, di(3-glycidoxypropyl) dimethoxysilane, vinyltriethoxysilane, vinyltris-2-methoxyethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, N-2-aminoethyl-3-propylmethyldimethoxysilane, N-2-aminoethyl-3-propyltrimethoxysilane, N-2-aminoethyl-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, tetraethoxysilane and the like.

The presence of the amine function appears to result in a stronger adsorption of the silane on the formation rock. The resultant polymer renders the treated portion of the formation less oil wet than when a non-amine-containing silane is employed. Thus, in subsequent production of oil through the formation, less oil is retained by the formation and more of the oil is produced.

For purposes of brevity and clarity, the terms "amine," "alkyl," "alkenyl," "aryl," and "carbhydryloxy" have been used above to describe substituents of organosilanes and alkoxides of organosilanes which are useful in the practice of the invention. It is to be understood that these substituents may themselves be substituted or unsubstituted and that each, except for aryl species, may be branched or unbranched.

Such organosilicon compounds are disclosed in U.S. Patent No. 4,580,633 and 4,708,207.

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The weight ratio of RPM macromolecule to organosilicon compound in the aqueous composition is generally from about 3:200 to about 20:4. The weight percentage of the RPM and organosilicon compound composite in the aqueous composition is generally from about 0.01 to about 25 weight percent.

5 For instance, where the RPM macromolecule is PVA, the concentration ratio in parts per million of PVA RPM macromolecule to silicon in the organosilicon compound in the aqueous composition is generally from about 20,000:80 to about 200,000:40,000, preferably from about 50,000:800 to about 100,000:4,000. The weight percentage of the PVA RPM and silicon in the
10 organosilicon compound composite in the aqueous composition is generally from about 2.0% to 24.00%, preferably from 5.0% to 10.5%, weight percentage. The concentration ratio in parts per million of polyacrylamide RPM macromolecule to silicon in the organosilicon compound in the aqueous composition is generally from about 100:80 to about 6,000:40,000, preferably
15 from about 900:800 to about 3,000:4,000. The weight percentage of the polyacrylamide RPM and silicon in the organosilicon compound composite in the aqueous composition is generally from about 0.02% to 4.60%, preferably from 0.17% to 0.70%, weight percent.

In one embodiment, a subterranean formation may be treated using the
20 disclosed aqueous composition by introducing the aqueous composition of the invention into the formation through a wellbore. Such a water control treatment fluid may be formulated with the aqueous composition and an aqueous base fluid. The weight percentage of aqueous composition being the RPM macromolecule and organosilane together in the composition of the
25 invention is generally about 0.01 to about 15.0 weight percent. As set forth in Example 1, the amount of combined RPM macromolecule and organosilicon compound in the aqueous composition of the invention may be between from about 0.02% to about 4.60%, preferably from about 0.17% to 0.70%, weight percentage.

30 With benefit of this disclosure, an aqueous base fluid may be any aqueous-base fluid suitable for well treatments known in the art including, but not limited to, fresh water, acidified water having pH range from 1.0 to 3.0,

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brine, sea water, synthetic brine (such as 2% KCl), produced formation water etc.

If so desired, optional mutual solvents may also be used with the aqueous composition of the invention. Mutual solvents, among other things, may act to remove hydrocarbons adhering to formation material. In this regard, any mutual solvent suitable for solubilizing hydrocarbons may be employed including, but not limited to, terpenes (such as limonene), C₃ to C₉ alcohols, glycol-ether (such as ethylene glycol monobutyl ether, "EGMBE"), or mixtures thereof.

It will be understood with benefit of the present disclosure that other additives known in the art for use in stimulation and well treatments may be employed in the practice of the disclosed method if so desired. For example, surfactants, thickeners, diversion agents, pH buffers, etc. may be used. In one embodiment, internal diverting materials may be employed if desired. Examples of suitable diverting agents include, but are not limited to, viscous water external emulsions, and are known to those of skill in the art. In one embodiment, an aqueous composition may be added to a salt solution, such as a 2% salt solution, wherein the salt is preferably potassium chloride.

The disclosed aqueous compositions may be used as the only component in an aqueous water control treatment fluid or may be combined with other components of stimulation fluid or other well treatment fluid (such as hydraulic fracturing fluids, acid fluids, surfactant squeeze treatment fluids, etc.).

It will also be understood with benefit of this disclosure that the disclosed aqueous composition may be mixed with an aqueous base fluid to form a "spearhead" fluid to precede the introduction of a stimulation fluid or other well treatment fluid. This may be done, for example, to achieve diversion of a stimulation fluid into hydrocarbon bearing areas of the formation by virtue of the copolymer's deleterious effect on permeability to water in water bearing areas of the formation. Alternatively, or additionally, the aqueous composition may follow such a well treatment fluid and/or be combined with the body of such a well treatment fluid, or used in any combination thereof. In any case,

the introduction of the aqueous composition into a subterranean formation in conjunction with a well treatment, such as a stimulation treatment, may be used to advantageously place the composition in a position to reduce production of water following the stimulation treatment. Examples of procedural details for use of water control materials in conjunction with well treatments may be found in U.S. Pat. No. 6,169,058.

Whether utilized as part of a stand-alone water control treatment fluid, employed in conjunction with another type of well treatment such as a stimulation treatment, or otherwise introduced into a well, the disclosed aqueous composition may be present in any concentration suitable for controlling water production in a subterranean formation. However, in one embodiment, one or more of the disclosed RPMs and organosilicon compounds are present in the treatment fluid at a total concentration of from about 500 ppm to about 10,000 ppm polymer, alternatively from about 1000 ppm to about 5,000 ppm polymer, based on the total weight of the water control treatment fluid.

To reduce injection pressures during injection of a well treatment fluid, the potassium chloride may be added to the aqueous solution and the pH reduced to a low value, for example to about 1, just prior to introduction of the treatment fluid into a wellbore. Using this optional procedure helps minimize injection pressure and ensure the extent of penetration of the aqueous composition into the formation. The pH of a well treatment fluid may be lowered by the addition of any acidic material suitable for decreasing pH of the fluid to less than about 3, and alternatively between about 1 and about 3. Suitable acidic materials for this purpose include, but are not limited to, hydrochloric acid, formic acid and acetic acid, etc. With benefit of this disclosure, those of skill in the art will understand that addition of acidic material and adjustment of pH may be varied as desired according to treatment fluid characteristics and formation temperature conditions in order to optimize polymer retention and water control.

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The aqueous composition may be batch prepared or prepared by continuous mix processes. For example, the water control treatment fluid may be first prepared in total, and then injected or otherwise introduced into a subterranean formation. This is referred to as a "batch mixing" process. In
5 another embodiment, a water control treatment fluid may be prepared by continuous mix processes, wherein the treatment fluid components are mixed together while the fluid is simultaneously introduced into the wellbore.

Once a treatment fluid is prepared (either by batch or continuous mixing), the water control treatment fluid is introduced into the subterranean
10 formation in any amount suitable for contacting a portion of a reservoir matrix of flow pathways. By "introduced" it is meant that a fluid may be pumped, injected, poured, released, displaced, spotted, circulated or otherwise placed within a well, wellbore, and/or formation using any suitable manner known in the art. In one embodiment, an amount of treatment fluid sufficient to treat the
15 entire height of the producing interval having a radius of from about 3 to about 10 foot from the wellbore may be employed, however greater or lesser amounts are also possible.

When employed in conjunction with a non-fracture treatment water control treatment fluid, introduction rates for either batch or continuous mixed
20 water control treatment fluids are typically held below flow rates that would cause pressures to exceed those necessary to fracture the formation being treated. In this regard, flow rates may be adjusted during treatment fluid introduction to ensure that pressures are maintained below those necessary for fracturing.

25 When used in conjunction with well treatments such as stimulation treatments, treatment fluid introduction flow rates typically depend on the nature of the treatment being performed. For example, in the case of a matrix acid treatment the disclosed copolymer compositions may be included in a "spearhead" fluid ahead of the acid treatment, in the acid treatment, or
30 following the acid treatment (or in any combination of steps before, in, or after the acid treatment), and are typically introduced at a rate below the flow rate necessary to fracture the formation in a manner similar to the rate employed

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for a water control treatment fluid injected alone. When used in conjunction with a hydraulic fracture treatment, fluid introduction rates (whether utilized as a spearhead, in the fracture treatment fluid, or both) are typically above rates that cause pressures to exceed those necessary to fracture a formation.

5 Whether employed as a stand-alone fluid or in a stimulation fluid (such as an acid fluid or hydraulic fracture fluid), similar concentrations of copolymer compositions are typically employed.

In one water control treatment embodiment for treating a subterranean formation in a production well, the well may be shut-in from about 6 to about

10 48 hours after introduction of a water control treatment fluid in order to allow maximum anchoring and retention of the aqueous composition. Following such a shut-in period, the well may be placed back on production. In another water control treatment embodiment for treating an injection well, a water control treatment fluid may be injected in a manner similar to that described

15 for treatment of a production well, with the exception that the injection well is not typically shut-in after injecting the treatment fluid, but is instead placed back on injection immediately. In this embodiment, the aqueous composition is expected to ultimately improve the water sweep efficiency in the reservoir by reducing water channeling from the injector to surrounding producing wells.

20 Such a condition may be the case, for example, in injection wells where water channeling is suspected to be occurring through high permeability streaks in the formation strata penetrated by the injection well.

With benefit of the present disclosure, it will be understood that the disclosed aqueous composition when placed in a subterranean formation may

25 induce an artificial pressure barrier and, in the case of the treatment of vertical coning problems, may be placed beyond the wellbore to an area beyond that influenced by the critical draw down pressure responsible for vertical water migration.

Although the disclosed method and compositions may be employed as

30 a water control treatment at any time in the producing life of a production well or the injection life of an injection well, it may be desirable to perform such treatment as soon as a coning or channeling problem (or potential coning or

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channeling problem) is identified, rather than waiting to the point where coning or channeling becomes severe.

In a preferred embodiment, permeability to water in a subterranean formation may advantageously be reduced without substantially reducing permeability to oil in the formation. In this regard, the measure of reduction of permeability of a subterranean formation to a given fluid may be expressed as the resistance factor, R_f . For example, the quotient of permeability to water at irreducible oil saturation prior to treatment (K_{wi}) to the permeability to water at irreducible oil saturation after treatment (K_{wf}) is defined herein as the resistance factor, R_f for water. In this regard, the disclosed methods and compositions are capable of achieving a water resistance factor, R_f , of greater than or equal to about 5, preferably greater than 8 or 9, measured at laminar flow rates of about 0.05 to 10.0 ml/min across a 2.5 cm diameter core.

Similarly, the quotient of permeability to oil at irreducible water saturation before treatment (K_{oi}) to permeability to oil at irreducible water saturation after treatment (K_{of}) is defined herein as the resistance factor, R_f , for oil. Advantageously, the disclosed method and compositions may be used to obtain an oil resistance factor, R_f , of from about 1 to about 2, alternatively from about 1 to about 1.5, and alternatively of less than about 2 at flow rates of about 0.05 to 6.0 ml/min across a 2.5 cm diameter core, at the same time the above-described water resistance factors are achieved.

Use of the aqueous compositions of the invention is applicable in high permeability producing wells previously not considered by RPM-containing compositions of the prior art. In a preferred embodiment, the aqueous compositions of the invention are used with a systematic approach consisting of proper pre-flushes and post-flushes. In a preferred embodiment, wells to be treated are produced from multi-layered sandstone formations with one or more layers that are still saturated with hydrocarbon. Otherwise distinct water and hydrocarbon production within the production interval(s) is desirable. Preferably, no cross-flow between layers exists.

The aqueous compositions of the invention have particular applicability in those instances where the formation permeability is between from about 0.1

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to about 8,000 md. In high permeability (>1 to 1.5 Darcy) formations, optimum treatment results have been obtained. Core flow test results show effectiveness at a permeability as high as 7.0 Darcy under high rate flow conditions.

5 If the RPM treatment is placed in homogeneous zones producing both water and hydrocarbon (fractional flow), both water and hydrocarbon permeability may be decreased significantly. Ideally, resistance to water flow will substantially exceed resistance to hydrocarbon (oil or gas) flow, following RPM treatment.

10 RPM treatment is ideally designed for radial penetration of 10 ft. However, as a practical matter, adequate treatment design may be for radial penetration of 5 to 8 ft. The RPM treatment can be bullheaded. However, it may be preferable to place the treatment through coiled tubing, especially in longer intervals.

15 The following examples will illustrate the practice of the present invention in its preferred embodiment. Other embodiments within the scope of the claims herein will be apparent to one skilled in the art from consideration of the specification and practice of the invention as disclosed herein. It is intended that the specification, together with the example, be
20 considered exemplary only, with the scope and spirit of the invention being indicated by the claims which follow.

EXAMPLES

 The Examples illustrate that the compositions of the invention are
25 highly effective in sandstone formations having absolute permeabilities to brine of 1.5 to 7.0 Darcy in that water flow relative to oil flow is significantly reduced in such high permeability sandstone cores. Unless specified to the contrary, all percentages herein refer to weight percentages.

Example 1.

30 The treatment fluid used in this test contains an RPM macromolecule concentrate containing 15% N-vinylformamide, 30% AMPS, 54.9% acrylamide

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and at most, about 0.1% methylenebisacrylamide packaged as a 3% polymer solution in 1% sodium chloride and the polymer has a Fikentcher K value of about 250 prior to the addition of salt. The treating fluid was prepared by diluting 3% (wt) of the RPM macromolecule concentrate in 2% aqueous potassium chloride and adding 0.5% (wt) organosilane binding agent, 3-aminopropyltriethoxysilane. The polymer solution is mixed well prior to use in the test.

Core flow tests were conducted on Berea core plug cylinders, measuring 1 in diameter and 3 inches in length, having N₂ permeabilities of 1000 md. The core plugs were evacuated with air and then saturated with 2% aqueous solution of potassium chloride (KCl). The core was then installed in a core holder. Approximately 200 psi back pressure was applied at the exit end and approximately 1,000 psi confining stress (overburden pressure) was applied around the entire cylinder. The confining stress pressure simulates stress in the downhole formation. After these pressures are applied and set, the temperature was elevated to 150°F. (simulation of the reservoir temperature). Sequential flows of water and oil were injected through the core as discussed in the paragraph below. The water composition was 2% KCl and the oil was a 50% (wt.) White Mineral Oil in Isopar LTM (Exxon). Each fluid was injected and pumped at a constant rate of between 0.3 ml/min to 5 ml/min. while measuring pressure drop along the length of the core. After obtaining a stable pressure differential, permeabilities were calculated using Darcy's equation for laminar flow through a cylindrical core:

$$k = Q \cdot m \cdot L / DP \cdot A$$

25

where

k = permeability to liquid, Darcies

Q = rate of flow, ml/sec

A = Area, cm²

m = viscosity, centipoises

30

L = length, cm

DP=pressure differential, atm.

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The water composition was first injected in a production direction. This simulates the production of water from the formation into the wellbore. The specific permeability to water (brine), k_w , md (absolute), is tabulated in Column III of Table I. After introduction of the White Mineral Oil in Isopar L solution, the effective permeability of the oil at residual oil saturation was then calculated, represented as k_o , md (before) in Column IV of Table I. The water composition was then injected in the production direction. Effective permeability to water at residual oil saturation, represented as k_w , md (before) in Column V of Table I, was then calculated. This is somewhat lower than first water measurement solution since this simulates water flowing through a previously oil saturated formation. Approximately 10 pore volumes of the treatment fluid (the solution of Example 1 in the water composition) was then injected in the reverse (injection) direction at a constant rate of 1 ml/min. (This simulates injection from the wellbore perforation into the formation.) A pore volume is the volume of fluid that the core can hold at complete fluid saturation. Shut-in of the treatment fluid at test temperature and confining pressure was allowed to occur for the designated shut-in period. The water solution was then injected in the production direction at a constant rate of 1 ml/min while collecting produced fluids and monitoring differential pressure. Flow was continued until a stable differential pressure was obtained. The effective permeability to water following treatment was then calculated, represented as k_w , md (after) in Column 6 of Table I. ISOPAR-L was then injected in the production direction at a constant rate of <10 ml/min. The effective permeability to oil following treatment, represented as k_o , md (after) in Column VI of Table 1 was then calculated.

Specific core flow tests were conducted on the water completion fluids of Example 1 at various levels of permeability, as high as 7.0 Darcy, under high rate flow conditions as follows:

The water composition was first injected in a production direction. This simulates the production of water from the formation into the wellbore. The specific permeability to water (brine), k_w , md (absolute), is tabulated in Column III of Table I. After introduction of the White Mineral Oil in Isopar L

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solution, the effective permeability of the oil at residual oil saturation was then calculated, represented as k_o , md (before) in Column IV of Table I. The water composition was then injected in the production direction. Effective permeability to water at residual oil saturation, represented as k_w , md (before) in Column V of Table I, was then calculated. This is somewhat lower than first water measurement solution since this simulates water flowing through a previously oil saturated formation. Approximately 10 pore volumes of the treatment fluid (the solution of Example 1 in the water composition) was then injected in the reverse (injection) direction at a constant rate of 1 ml/min. (This simulates injection from the wellbore perforation into the formation.) A pore volume is the volume of fluid that the core can hold at complete fluid saturation. Shut-in of the treatment fluid at test temperature and confining pressure was allowed to occur for the designated shut-in period. The water solution was then injected in the production direction at a constant rate of 1 ml/min while collecting produced fluids and monitoring differential pressure. Flow was continued until a stable differential pressure was obtained. The effective permeability to water following treatment was then calculated, represented as k_w , md (after) in Column 6 of Table I. ISOPAR-L was then injected in the production direction at a constant rate of <10 ml/min. The effective permeability to oil following treatment, represented as k_o , md (after) in Column VI of Table 1 was then calculated.

Specific core flow tests were conducted on the water completion fluids of Example 1 at various levels of permeability, as high as 7.0 Darcy, under high rate flow conditions as follows:

- Run 1 (Comparative). 6% RPM macromolecule concentrate in the treating fluid (without organosilane agent) - 4.5 D core
- Run 2: 6% RPM macromolecule concentrate in the treating fluid with organosilane - 1.5 D core
- Run 3: 6% RPM macromolecule concentrate in the treating fluid with organosilane - 1.7 D core
- Run 4: 6% RPM macromolecule concentrate in the treating fluid with organosilane - 7.0 D core

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Run 5: 6% RPM macromolecule concentrate in the treating fluid with organosilane – 5.0 D core

The test results are summarized in Table 1. To screen effectiveness in reducing relative permeability to water only, oil permeabilities were not measured in Runs 1-4. Once the effectiveness of the Water Control treating fluid system was determined, the effect on oil permeability was measured with Run 5. Post-treatment shut-in time, concentrations of the Water Completion Fluid and effects of buffering the system (from pH > 9 to between 7 and 8) were also varied to maximize treatment effectiveness in reducing permeability to water while maintaining adequate oil permeability.

Table 1							
I. Run No.	II. Fluid Tested	III. kw, md (absolute)	IV. ko, md (before)	V. kw, md (before)	VI. kw, md (after)	VII. ko, md (after)	VIII. R _w / R _o
1	6% RPM Concentrate	4480	---	4480	1014	---	4.4 / --
2	6% RPM Concentrate and Organosilane	1500	---	1500	80	---	18.8 / --
3 ⁽¹⁾	6% RPM Concentrate and Organosilane	1700	---	1700	180	---	9.4 / --
4	6% RPM Concentrate and Organosilane	7000	4500	870	151	2255	5.8 / 2.0
5 ⁽²⁾	6% RPM Concentrate and Organosilane (buffered)	4953	---	4953	170	---	29.1 / --

1. Permeability = 400 md after 24-hour shut-in; reduced to 180 md after 72 hours.

2. Permeability = 170 md after 72-hour shut-in; increased to 225 md after 84 hours.

All Runs were conducted at 150°F and post-treatment shut-in time of 72 hours

15 – unless noted.

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System pH buffered to 7.4 (to increase long-term treatment solution stability).

Runs 1 through 5 were evaluations of 6% Water Control treating Fluid containing 1% by volume of the organosilane , 3-aminopropyltriethoxysilane solution). Tests resulted in no less than 76% reduction in permeability to water in any case. Run 4 illustrates the effect of Water Completion Fluid on the relative permeability to oil, as well as to water. After a 72-hour shut-in period, an 83% reduction in permeability to water was followed by a 50% return permeability to oil. Return oil permeability reached a point at which the value seemed to stabilize and the test was halted. Continuation of the flow stage might have resulted in even higher return values.

In Run 4, the oil flow stage permeability continued to increase with time until it reached a point where the values seemed to stabilize. Continuing oil flow might have possibly increased the value over a longer time period. Reduction in oil permeability was similar to the reduction in brine permeability, indicating excess binding agent relative to Water Control treating Fluid concentration in this specific test case. Initial oil permeability was nearly twice the absolute brine permeability – anomalous among the Berea cores used by both laboratories in this study. Typically, initial oil permeability is less than absolute brine permeability.

Run 5 was also performed using a buffered Water Control treating Fluid system. A low pH buffer was used to reduce the final pH of the system from over 9 to between 7 and 8. Lowering the pH of the system resulted in a higher reduction in permeability to water when comparing test results where core permeability, treatment concentration and shut-in time were relatively similar. Runs 4 and 5 were used for this comparison. Absolute permeabilities were 7000 and 4953 md respectively. After the 72-hour shut-in time, the buffered system (Run 5) resulted in a 97% reduction in permeability to water compared to 83% for the non-buffered system.

In each case, permeabilities to water were measured, and the resistance factor to water was calculated. In those tests in which oil pre- and

post-treatment oil permeabilities were measured, resistance factor to oil was also calculated. Resistance factors (Rf) are calculated as follows:

$$\text{Rf Water} = \frac{k_w (\text{BT})}{k_w (\text{AT})}$$

$$\text{Rf Oil} = \frac{k_o (\text{BT})}{k_o (\text{AT})}$$

5 where k_w = permeability to water (brine) at residual oil saturation

k_o = permeability to oil at residual water (brine) saturation

BT = Before Treatment with RPM

AT = After Treatment with RPM

10 High Rf Water (> 5-10) relative to Rf Oil (< 2-2.5) is desirable. If water permeability is completely shut off ($k_w (\text{AT}) = 0$), then Rf Water = ∞.

Results of these tests indicates that the Water Treatment Fluid of Example 1 effectively reduced relative permeability to water in high permeability sandstones.

15 Example 2.

Core flow tests were conducted on Berea core plug cylinders, measuring 1 in diameter and 3 inches in length, having N_2 permeabilities of 1000 md. The core plugs were evacuated with air and then saturated with a simulated formation brine comprising a mixture of 2% potassium chloride (KCl), 5% sodium chloride (NaCl) and 1% calcium chloride ($CaCl_2$). Each sample was installed in a specially designed core holder, with a pressure tap at 1 inch from the injection face, which was located in an air bath oven. In addition, approximately 200 psi back pressure was applied at the exit end and approximately 1,000 psi confining stress (overburden pressure) was applied around the entire cylinder. The temperature was then elevated to 150°F. and the test brine was then injected in the production direction at a constant rate (<10 ml/min) while the produced fluids were collected and differential pressure versus time was monitored. Specific permeability to brine was then calculated for each section of the core (Section 1 being one inch penetration and Section 2 being the remainder of the core). An oil blend of a 50:50 weight mixture of ISOPAR-L:Chevron Superla® White Oil was then injected in the production direction at stepwise increasing rates while produced fluids were collected

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and differential pressure was monitored until an equilibrium permeability was established at each rate level. Effective permeability to oil at initial water saturation versus injection pressure data was calculated for each section of the core. Test brine was then injected in the production direction at stepwise
5 increasing rates while collecting produced fluids and monitoring differential pressure and elapsed time until an equilibrium permeability was established at each rate level. Effective permeability to water at residual oil saturation versus injection pressure data was calculated for each section of the core. Approximately 10 pore volumes of the treatment fluid of Example 1 was
10 injected in the injection direction at a constant rate of 0.3 ml/min while produced fluids were collected and differential pressure was monitored. The sample was then shut in with the treatment fluid in place for 24 hours. The test brine was then injected in the production direction at stepwise increasing rates while the produced fluids were collected and differential pressure was
15 monitored until an equilibrium permeability was established at each rate level. Effective permeability to water at residual oil saturation versus injection pressure data was calculated for each section of the core. An oil blend of 50:50 weight mixture of ISOPAR-L:Chevron Superla White Oil was then injected in the production direction at stepwise increasing rates while
20 produced fluids were collected and differential pressure was monitored until an equilibrium permeability was established at each rate level. Effective permeability to oil at initial water saturation versus injection pressure data were calculated for each section of the core. Additional test brine was then injected in the production direction, differential pressure monitored, effective
25 permeability calculated and oil blend injected in the production direction and effective permeability to oil at initial water saturation versus injection pressure data was calculated for each section of the core. Return permeability to water and oil data for each section for each cycle was then calculated.

Results of these core flow screening tests indicated that the
30 composition of the invention effectively reduced relative permeability to water in high permeability sandstones. The results confirm that the Water Control treating Fluid of the invention was most effective under the test conditions of

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150° F and over 2-3 Darcy permeability. Treatment effectiveness was sufficiently retained as flow differential pressure was increased – unprecedented in cores with greater than Darcy permeability.

Three tests with high permeability Berea cores were undertaken. Results are summarized in FIGs. 1, 2 and 3. In each test, permeabilities to oil and water were measured in two core sections. The first section (wellbore) was 1" penetration distance, and the second section (formation) was the remaining core length. Cores were typically about 4" long. Permeabilities were measured at stepwise increasing rates. Core section permeabilities were measured at rates corresponding to 30-40 psi/ft. Core section permeabilities measured at the highest rate for each flow step are graphically reported.

Under these tests, the Water Control treating Fluid system of Example 1 did not contain buffer to reduce pH to between 7 and 8. Such buffer may increase effectiveness further, as indicated in Example 2.

Test 1. In Test 1, a low concentration Water Completion Fluid system of Example 1 was evaluated (containing 3% Water Control treating Fluid, 0.5% organosilane, 3-aminopropyltriethoxysilane solution in aqueous 2% KCl solution). The treatment was effective in significantly decreasing the relative permeability to water in both sections of the Berea core – nearly completely shutting off water flow. The substantial reduction in permeability was retained during the second cycle injection, indicating binding agent effectiveness. The effective permeability to oil was reduced to about 40-45% of the original permeability. This translates to an Rf Oil value of about 1.7. Flow performance following the second oil cycle was similar; also showing an increase in oil permeability. The results are reported in FIG. 1.

Test 2. In Test 2, a 4% Water Control treating Fluid of Example 1 containing approximately 0.3% of organosilane, 3-aminopropyltriethoxysilane solution was employed. The treatment did not reduce relative permeability to water in the sections of the core (overall 41 percent of initial value) – apparently due to the reduced level of binding agent used. However, this degree of permeability reduction (Rf Water ~2.5) was retained during the second cycle injection –

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which would not be expected with Water Control treating Fluid alone at this high permeability level. The effective permeability to oil was reduced, but to acceptable levels of 63.4 percent and 66.1 percent initial value overall after cycles 1 and 2, respectively (R_f Oil ~ 1.5).

- 5 Test 3. In Test 3, a 5% Water Control treating Fluid system of Example 1 was tested. The binding agent concentration was increased to the level used in Test 1, following the results of Test 2. The 5% Water Control treating Fluid treatment reduced relative permeability to water significantly (overall 17.5 percent of initial value). More importantly, the degree of
10 reduction in brine permeability was retained during the second cycle injection. The effective permeability to oil was only modestly reduced in this case (to 74.8 percent of initial value in both flow cycles).

In summary, the Water Control treating Fluid of the invention is effective in reducing water flow relative to oil in very high permeability
15 sandstone (>1.5 Darcy) – extending the previous estimated practical permeability application range of Water Control treating Fluids without organosilanes.

Results of flow testing in high permeability Berea cores indicate that treatment with the inventive Water Completion Fluid system significantly
20 reduced water flow relative to oil flow – and maintained effectiveness with repeated flow cycles – indicating binding agent effectiveness.

From the foregoing, it will be observed that numerous variations and modifications may be effected without departing from the true spirit and scope of the novel concepts of the invention.

1. A method for reducing or eliminating the production of water in an oil or gas well penetrating a subterranean formation by:

introducing into the well an aqueous composition comprising a mixture of:

(a) an organosilicon compound which forms a water-soluble silanol by hydrolysis as well as binds to the formation substrate minerals; and

(b) a relative permeability modifier (RPM) macromolecule which impedes the production of water wherein the RPM macromolecule has at least one attachment site for the organosilicon compound; and

reducing or eliminating the production of water in the well without substantially affecting the production of hydrocarbons.

2. The method of Claim 1, wherein the concentration of RPM in the aqueous composition is between from 100 to 80,000 ppm.

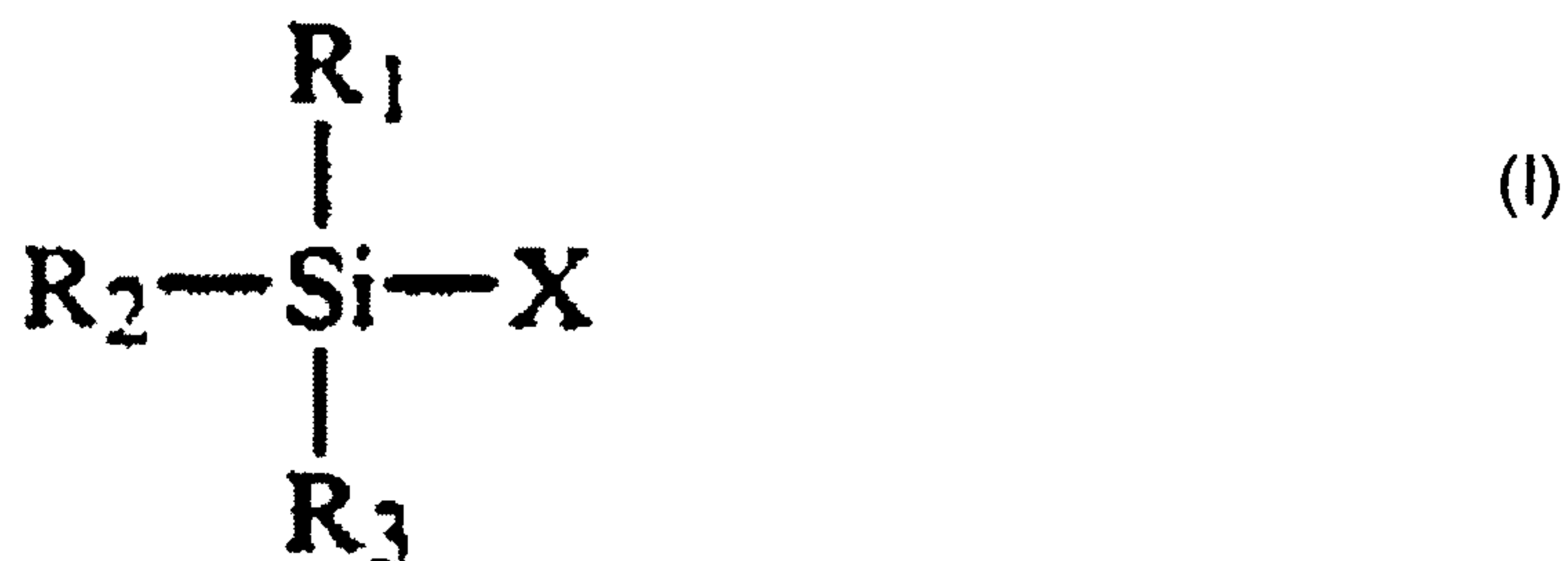
3. The method of Claim 1, wherein the concentration of organosilicon compound in the aqueous composition is between from 500 to 20,000 ppm.

4. The method of Claim 1, wherein the organosilicon compound is vinyl tris-(2-methoxyethoxy) silane.

5. The method of Claim 1, wherein the formation substrate minerals include quartz, clay, shale, silt, chert, zeolite, or a combination thereof.

6. The method of Claim 1, wherein the formation permeability in the oil or gas well is between from 0.1 to 8,000 mD.

7. The method of Claim 1, wherein the organosilicon compound is an organosilane halide of the formula:



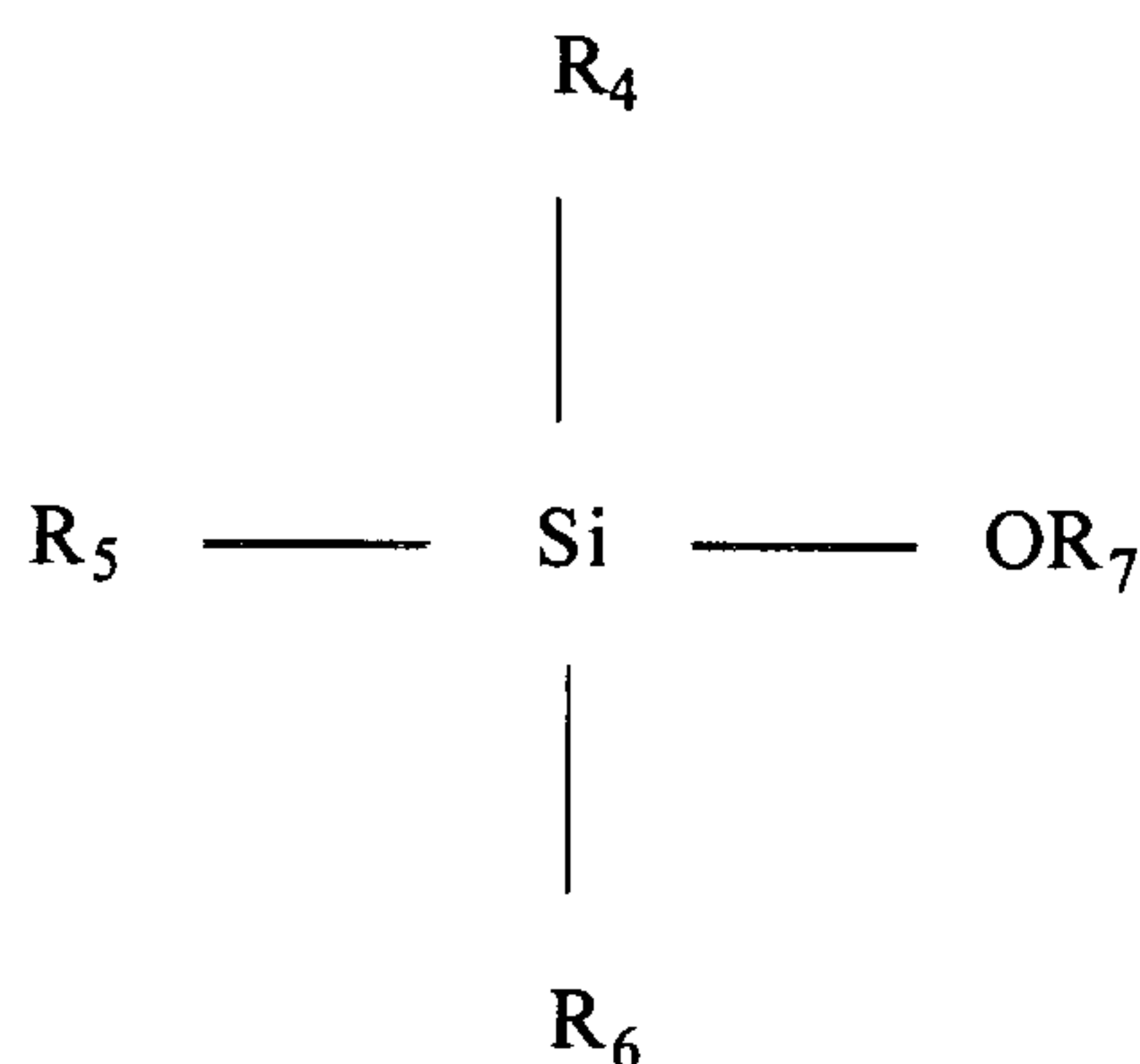
wherein X is a halogen, R₁ is an organic radical having from 1 to 50 carbon atoms, and R₂ and R₃ are the same or different halogens or organic radicals having from 1 to 50 carbon atoms.

5 8. The method of Claim 7, wherein X is a halogen selected from the group consisting of chlorine, bromine and iodine, R₁ is an alkyl, alkenyl, alkoxide or aryl group having from 1 to 18 carbon atoms and R₂ and R₃ are the same or different halogens selected from the group consisting of chlorine, bromine and iodine or alkyl, alkenyl, alkoxide or aryl group having from 1 to 18 carbon atoms.

10 9. The method of Claim 8, wherein X is chlorine.

 10. The method of Claim 7, wherein the organosilane halide is selected from methyldiethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, dimethyldibromosilane, diethyldiiodosilane, dipropyldichlorosilane, dipropyldibromosilane, butyltrichlorosilane, phenyltribromosilane, 15 diphenyldichlorosilane, tolyltribromosilane, propyldimethoxychlorosilane and methylphenyldichlorosilane.

 11. The method of Claim 1, wherein the organosilicon compound is an organosilane alkoxide of the formula:



20

wherein R₄, R₅ and R₆ are independently selected from hydrogen and organic radicals having from 1 to 50 carbon atoms, provided not all of R₄, R₅ and R₆ are hydrogen; and R₇ is an organic radical having from 1 to 50 carbon atoms.

12. The method of Claim 11, wherein R_4 , R_5 and R_6 are independently selected from hydrogen, amine, alkyl, alkenyl, aryl and carbhydroxy groups having from 1 to 18 carbon atoms, with at least one of the R_4 , R_5 and R_6 groups not being hydrogen, and R_7 is selected from amine, alkyl, alkenyl, and aryl groups having from 1 to 18 carbon atoms.

13. The method of Claim 1, wherein the RPM macromolecule has a molecular weight between from 50,000 to 20,000,000 g/mole.

14. The method of Claim 13, wherein the RPM macromolecule has a molecular weight between from 100,000 to 5,000,000 g/mole.

15. The method of Claim 14, wherein the RPM macromolecule has a molecular weight between from 250,000 to 2,000,000 g/mole.

16. The method of Claim 1, wherein the RPM macromolecule is derived from acrylamide.

17. The method of Claim 16, wherein the RPM macromolecule is a homopolymer or copolymer of acrylamide which has been sulfonated or quaternized.

18. The method of Claim 16, wherein the RPM macromolecule is a copolymer of acrylamide and at least one monomer selected from acrylic acid, (meth)acrylic acid, dimethyldiallylammonium chloride, acrylamidoethyltrimethylammonium chloride, methacrylamidoethyltrimethylammonium chloride, acrylamidomethylpropanesulfonic acid, N-vinyl pyrrolidone, N-vinyl formamide, N-vinyl acetamide, N-vinylmethacetamide, acrylamidoethyltrimethylammonium chloride, vinyl sulfonic acid, maleic acid, itaconic acid, styrene sulfonic acid, vinylsulfonic acid, methylenebisacrylamide and vinylphosphonic acid and sulfonate monomers thereof.

19. The method of Claim 1, wherein the RPM macromolecule is a polyvinylalcohol or polysiloxane.

20. The method of Claim 19, wherein the polyvinylalcohol has a degree of hydrolysis between from 50% to 100%.

21. The method of Claim 1, wherein the RPM macromolecule is a hydrophilic polymer selected from natural gums and a chemically modified
5 derivative thereof.

22. The method of Claim 21, wherein the RPM macromolecule is guar, carrageenan, gum Arabic, gum ghatti, karaya, tragacanth, pectin, starch, locust bean gum, scleroglucan, tamarind, xanthan gums or a hydroxyethyl, hydroxypropyl, hydroxypropylcarboxymethyl, hydroxyethylcarboxymethyl,
10 carboxymethyl or methyl cellulose derivative.

23. A method for controlling water by treating a subterranean formation in a production well, comprising introducing a water control treatment fluid into said formation through said production well, said water control treatment fluid comprising:

15 (a) an organosilicon compound comprising an organosilane halide or an organosilane alkoxide; and

(b) a relative permeability modifier (RPM) macromolecule which selectively impedes the production of water

wherein said water control treatment fluid is introduced at a flow rate less than
20 that necessary to fracture said formation and further wherein the water control treatment fluid substantially reduces permeability to water within the formation without substantially reducing permeability to oil within the formation.

24. The method of Claim 23, wherein the organosilicon compound binds both to the RPM macromolecule as well as to formation substrate minerals.

25 25. The method of Claim 24, wherein the formation substrate minerals include quartz, clay, shale, silt, chert, zeolite, or a combination thereof.

26. The method of Claim 23, wherein the formation permeability in the subterranean formation is from 0.1 to 8,000 mD.

27. A method for treating a subterranean formation, comprising:

(a) introducing a water control treatment fluid into said formation, said water control treatment fluid comprising:

(i.) an organosilicon compound comprising an organosilane halide or an organosilane alkoxide; and

5 (ii.) a relative permeability modifier (RPM) macromolecule which selectively impedes the production of water without substantially reducing permeability to oil within the formation

wherein said water control treatment fluid is introduced into said subterranean formation prior to, together with, or following a hydraulic fracturing or stimulation
10 fluid into said subterranean formation.

28. The method of Claim 27, wherein the organosilicon compound binds both to the RPM macromolecule as well as to formation substrate minerals.

29. The method of Claim 28, wherein the formation substrate minerals include quartz, clay, shale, silt, zeolite or a combination thereof.

15 30. The method of Claim 27, wherein the formation permeability ranges from 0.1 to 8,000 mD.

31. A method of treating a subterranean water injection well by introducing a treatment fluid into said water injection well, said treatment fluid comprising:

20 (a) an organosilicon compound which forms a water-soluble silanol by hydrolysis; and

(b) a relative permeability modifier (RPM) macromolecule which selectively reduces the permeability of the primary water pathway within the formation

25 wherein said treatment fluid is introduced at a flow rate below that necessary to fracture said formation.

32. The method of Claim 31, wherein the organosilicon compound binds both to the RPM macromolecule as well as to formation substrate minerals.

33. The method of Claim 32, wherein the formation substrate minerals include quartz, clay, shale, silt, chert, zeolite, or a combination thereof.

34. The method of Claim 31, wherein the formation permeability of the subterranean water injection well is from 0.1 to 8,000 mD.

5 35. The method of Claim 1, wherein the organosilicon compound and RPM macromolecule is present in the aqueous composition in an amount selected to impart a resistance factor for water of greater than 5 and a resistance factor for oil of less than 2, each of said water and oil resistance factors being measured at a laminar stable flow rate at constant pressure.

10 36. The method of Claim 27, wherein the water control treatment is introduced into the formation at flow rates below a flow rate that would cause pressures to exceed those necessary to fracture the formation.

37. The method of Claim 1, wherein the aqueous composition is a stimulation fluid.

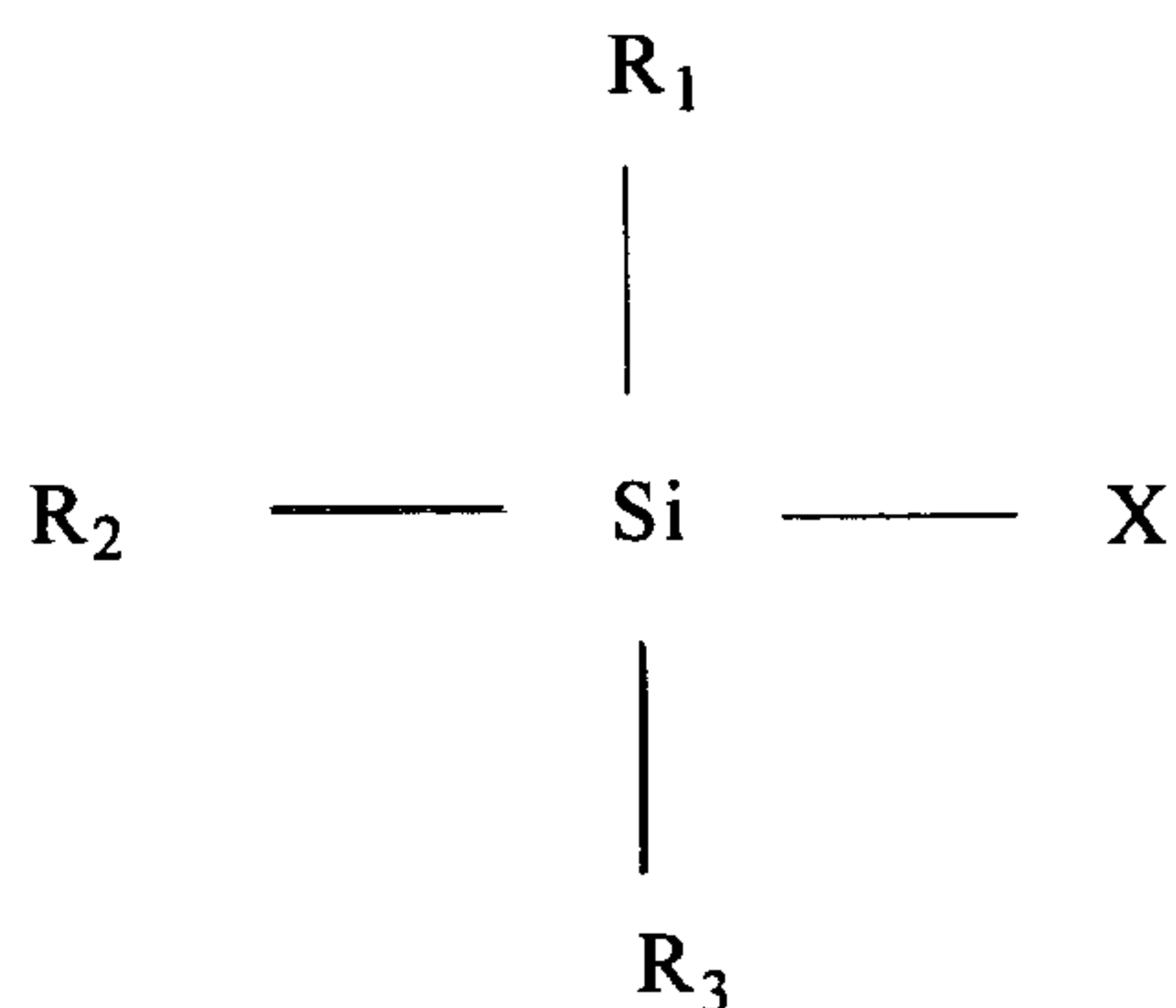
15 38. The method of Claim 23, wherein the water control treatment fluid is introduced into the subterranean formation prior to, together with, or following a stimulation fluid.

39. The method of Claim 23, wherein the water control treatment fluid further comprises a mutual solvent.

20 40. The method of Claim 35, wherein the resistance factor for water is greater than 8.0.

41. An aqueous well treatment fluid useful for selective permeability modification of a subterranean formation to control the production of water comprising a mixture of:

25 (a) an organosilicon compound which forms a water soluble silanol by hydrolysis and binds to the formation substrate minerals in the formation, wherein the organosilicon compound is selected from the group consisting of amino silanes and organosilane halides of the formula:



wherein X is halogen, R_1 is an organic radical having from 1 to 50 carbon atoms, and R_2 and R_3 are the same or different halogens or organic radicals having from 1 to 50 carbon atoms; and

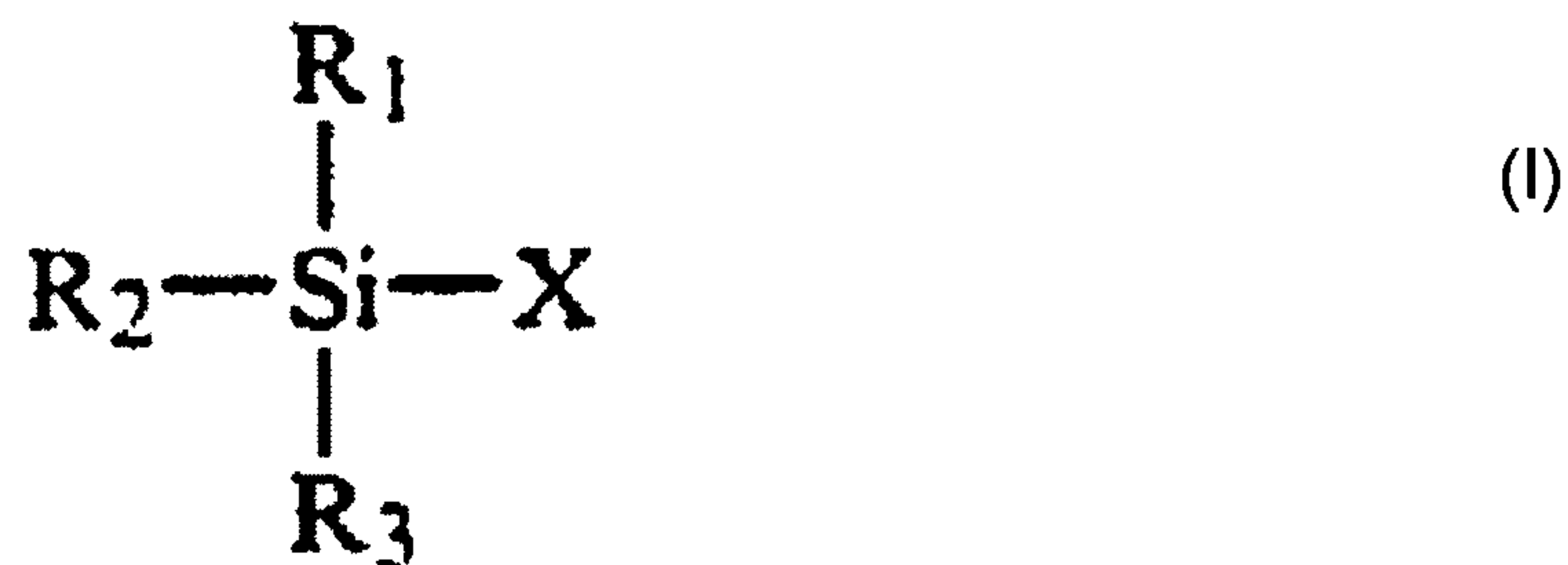
- (b) a relative permeability modifier (RPM) macromolecule which impedes the production of water, wherein the RPM macromolecule has at least one attachment site for the organosilicon compound
- and further wherein the fluid reduces or eliminates the production of water in the well without substantially affecting the production of hydrocarbons.

42. The well treatment fluid of Claim 41, wherein the concentration of RPM macromolecule in the water treatment fluid is between from about 100 to about 80,000 ppm.

43. The well treatment fluid of Claim 41, wherein the concentration of organosilicon compound is between from about 500 to about 20,000 ppm.

44. The well treatment fluid of Claim 41, wherein the organosilicon compound binds both to the RPM as well as formation substrate minerals in the well.

45. The well treatment fluid of Claim 41, wherein the organosilicon compound is an organosilane halide of the formula:



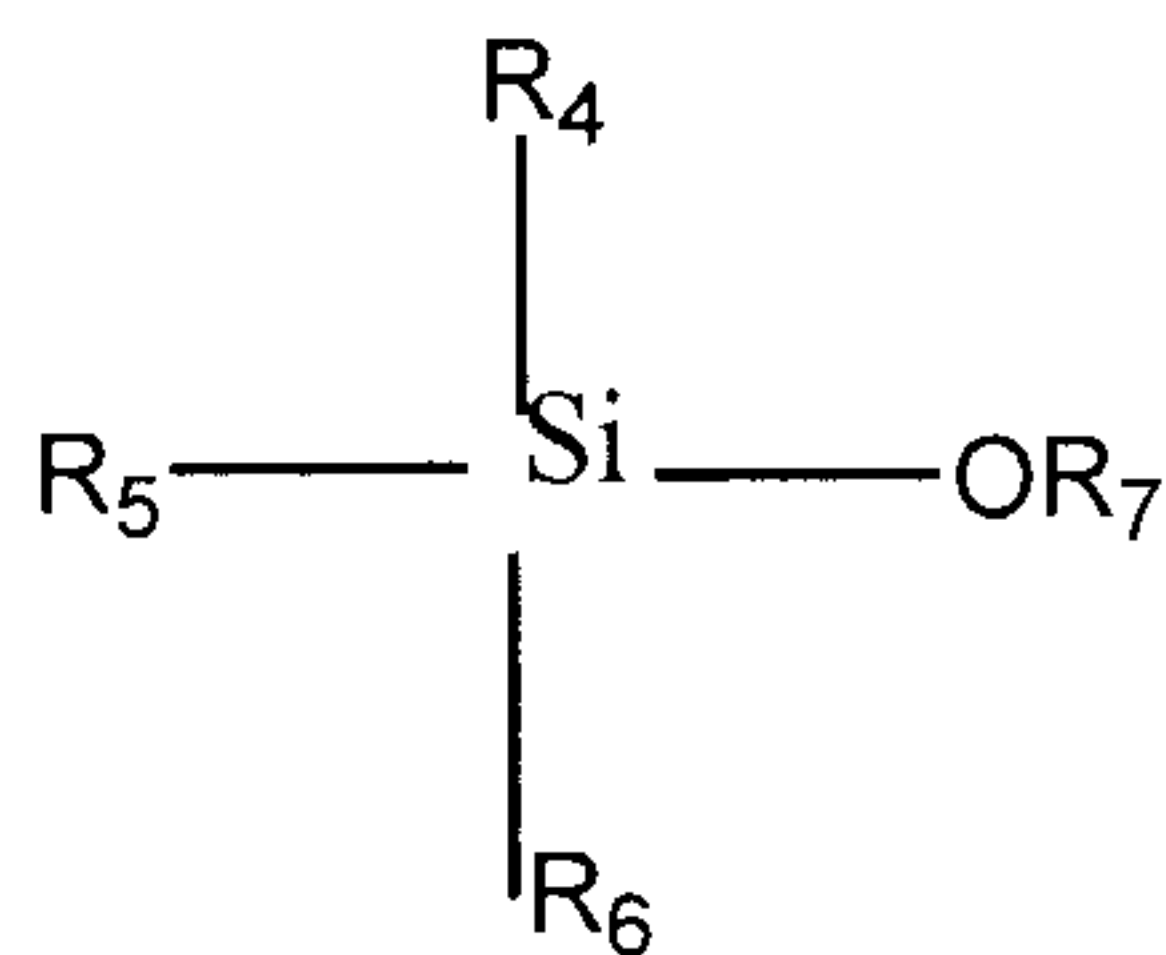
wherein X is a halogen, R₁ is an organic radical having from 1 to 50 carbon atoms, and R₂ and R₃ are the same or different halogens or organic radicals
 5 having from 1 to 50 carbon atoms.

46. The well treatment fluid of Claim 45, wherein X is a halogen selected from the group consisting of chlorine, bromine and iodine, R₁ is an alkyl, alkenyl or aryl group having from 1 to about 18 carbon atoms and R₂ and R₃ are the same or different halogens or alkyl, alkenyl or aryl group having from 1 to
 10 about 18 carbon atoms.

47. The well treatment fluid of Claim 46, wherein X is chlorine.

48. The well treatment fluid of Claim 41, wherein the organosilicon compound is an organosilane halide selected from methyldiethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, dimethyldibromosilane, diethyldiiodosilane, dipropyldichlorosilane, dipropyldibromosilane,
 15 butyltrichlorosilane, phenyltribromosilane, diphenyldichlorosilane, tolyltribromosilane, propyldimethoxychlorosilane and methylphenyldichlorosilane.

49. The well treatment fluid of Claim 41, wherein the organosilicon compound is an organosilane alkoxide of the formula:



(II)

wherein R_4 , R_5 and R_6 are independently selected from hydrogen and organic radicals having from 1 to about 50 carbon atoms, provided not all of R_4 , R_5 and R_6 are hydrogen and R_7 is an organic radical having from 1 to about 50 carbon atoms.

50. The well treatment fluid of Claim 49, wherein R_4 , R_5 and R_6 are independently selected from hydrogen, amine, alkyl, alkenyl, aryl and carbohydroxyl groups having from 1 to about 18 carbon atoms, with at least one of the R_4 , R_5 and R_6 groups not being hydrogen and R_7 is selected from amine, alkyl, alkenyl, and aryl groups having from 1 to about 18 carbon atoms.

51. The well treatment fluid of Claim 41, wherein the RPM macromolecule has a molecular weight between from about 50,000 to about 20,000,000 g/mole.

52. The well treatment fluid of Claim 51, wherein the RPM macromolecule has a molecular weight between from about 100,000 to about 5,000,000 g/mole.

53. The well treatment fluid of Claim 52, wherein the RPM macromolecule has a molecular weight between from about 250,000 to about 2,000,000 g/mole.

54. The well treatment fluid of Claim 41, wherein the RPM macromolecule is derived from acrylamide.

55. An aqueous well treatment fluid useful for selective permeability modification of a subterranean formation to control the production of water comprising a mixture of:

5 (a) an organosilicon compound which forms a water soluble silanol by hydrolysis and binds to the formation substrate minerals in the formation; and

10 (b) a relative permeability modifier (RPM) macromolecule which impedes the production of water, wherein the RPM macromolecule has at least one attachment for the organosilicon compound and is a homopolymer or copolymer of acrylamide which has been sulfonated or quaternized and further wherein the fluid reduces or eliminates the production of water in the well without substantially affecting the production of hydrocarbons.

56. The treatment fluid of Claim 41, wherein the RPM macromolecule is a copolymer of acrylamide and at least one monomer
15 selected from acrylic acid, (meth)acrylic acid, dimethyldiallylammonium chloride, acrylamidoethyltrimethylammonium chloride, methacrylamidoethyltrimethylammonium chloride, acrylamidomethylpropanesulfonic acid, N-vinyl pyrrolidone, N-vinyl formamide, N-vinyl acetamide, N-vinylmethylacetamide,
20 acrylamidoethyltrimethylammonium chloride, vinyl sulfonic acid, maleic acid, itaconic acid, styrene sulfonic acid, methylenebisacrylamide, vinylsulfonic acid and vinylphosphonic acid and sulfonate monomers thereof.

57. The well treatment fluid of Claim 41, wherein the RPM
25 macromolecule is a polyvinylalcohol or polysiloxane.

58. The well treatment fluid of Claim 57, wherein the polyvinylalcohol has a degree of hydrolysis between from about 50% to about 100%.

59. The well treatment fluid of Claim 41, wherein the RPM macromolecule is a hydrophilic polymer selected from natural gums and a chemically modified derivative thereof.

60. The well treatment fluid of Claim 59, wherein the RPM
5 macromolecule is guar, carrageenan, gum Arabic, gum ghatti, karaya, tragacanth, pectin, starch, locust bean gum, scleroglucan, tamarind, xanthan gums or hydroxyethyl, hydroxypropyl, hydroxypropylcarboxymethyl, hydroxyethylcarboxymethyl, carboxymethyl or methyl cellulose derivative.

61. An aqueous water control treatment fluid useful for selective
10 permeability modification of a subterranean formation comprising a mixture of:

(a) an organosilicon compound which forms a water soluble silanol by hydrolysis; and

(b) a relative permeability modifier (RPM) macromolecule having a
15 molecular weight between from about 50,000 to about 20,000,000 g/mole.

62. The aqueous water control treatment fluid of Claim 61, wherein the RPM macromolecule has a molecular weight between from about 100,000 to about 5,000,000 g/mole.

63. The aqueous water control treatment fluid of Claim 62, wherein the
20 RPM macromolecule has a molecular weight between from about 250,000 to about 2,000,000 g/mole.

64. A method for treating a subterranean formation penetrated by an oil or gas well, comprising introducing an aqueous water control treatment fluid into the formation the aqueous water control treatment fluid
25 comprising an organosilicon compound which forms a water soluble silanol by hydrolysis and a relative permeability modifier (RPM) macromolecule which impedes the production of water and having a molecular weight between from 50,000 to 20,000,000 g/mole, wherein production of water in

the well is reduced or eliminated without substantially affecting the production of hydrocarbons.

65. The method of Claim 64, wherein the organosilicon compound binds both to the RPM macromolecule as well as to formation substrate minerals.

5 66. The method of Claim 64, wherein the formation substrate minerals include quartz, clay, shale, silt, zeolite or a combination thereof.

67. The method of Claim 64, wherein the formation permeability ranges from 0.1 to 8,000 mD.

68. A method for treating a subterranean formation or an oil or gas well,
10 comprising introducing into the formation or oil or gas well an aqueous water control treatment fluid which reduces or eliminates the production of water in the well without substantially affecting the production of hydrocarbons, the fluid comprising a mixture of (i) an organosilicon compound which forms a water soluble silanol by hydrolysis and binds to the formation substrate minerals in the
15 formation and (ii) a relative permeability modifier (RPM) having at least one attachment site for the organosilicon compound and selected from the group consisting of polyvinyl alcohols and polysiloxanes.

69. The method of Claim 68, wherein the water control treatment fluid is introduced into said subterranean formation prior to, together with, or following
20 a hydraulic fracturing or stimulation fluid into said subterranean formation.

70. The method of Claim 68, wherein the organosilicon compound binds both to the RPM macromolecule as well as to formation substrate minerals.

71. The method of Claim 68, wherein the formation substrate minerals include quartz, clay, shale, silt, zeolite or a combination thereof.

25 72. The method of Claim 68, wherein the formation permeability ranges from 0.1 to 8,000 mD.

73. A method for reducing or eliminating the permeability to water in a sandstone formation which comprises introducing into the formation an aqueous composition comprising a mixture of:

(a) an organosilicon compound which forms a water-soluble silanol by hydrolysis; and

(b) a relative permeability modifier (RPM) macromolecule

wherein the aqueous composition is relatively non-damaging to oil permeability in the oil saturated zones while decreasing water permeability in the water saturated zones of the sandstone.

74. The method of Claim 73, wherein the concentration of organosilicon compound is between from 500 to 20,000 ppm.

75. The method of Claim 73, wherein the organosilicon compound binds both to the RPM as well as formation substrate minerals.

76. The method of Claim 73, wherein the sandstone permeability in the oil or gas well is between from 0.1 to 8,000 mD.

77. The method of Claim 76, wherein the sandstone permeability is greater than 1.5 Darcy.

78. The method of Claim 41, wherein the amino silane is selected from the group consisting of 3-aminopropyltriethoxy silane, N-2-aminoethyl-3-aminopropyltrimethoxy silane and aminoethyl-3-propylmethyldimethoxysilane.

79. The method of Claim 41, wherein the organosilicon compound is a vinyl silane.

80. The method of Claim 79, wherein the vinyl silane is vinyl tris-(2-methoxyethoxy) silane.

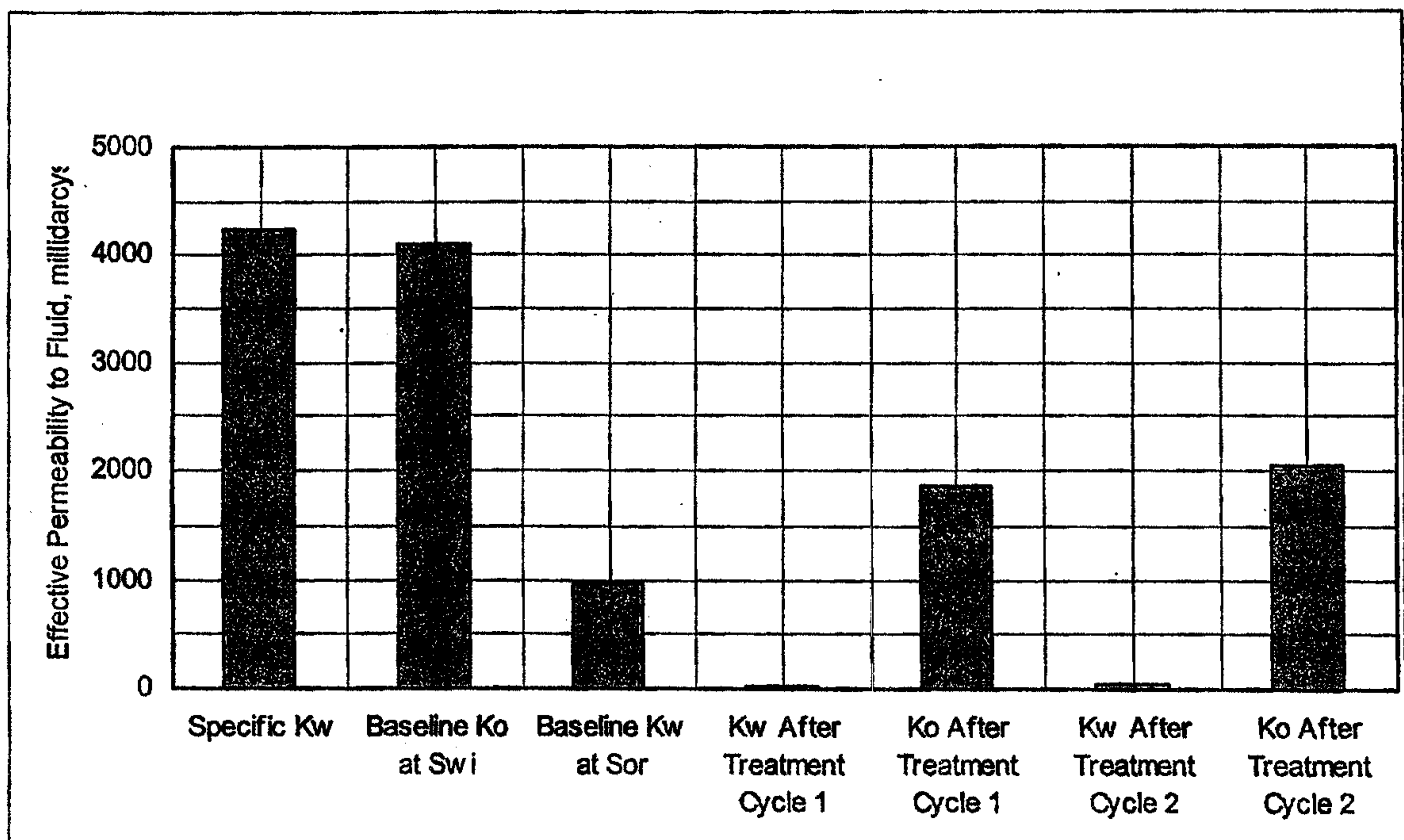


FIG. 1

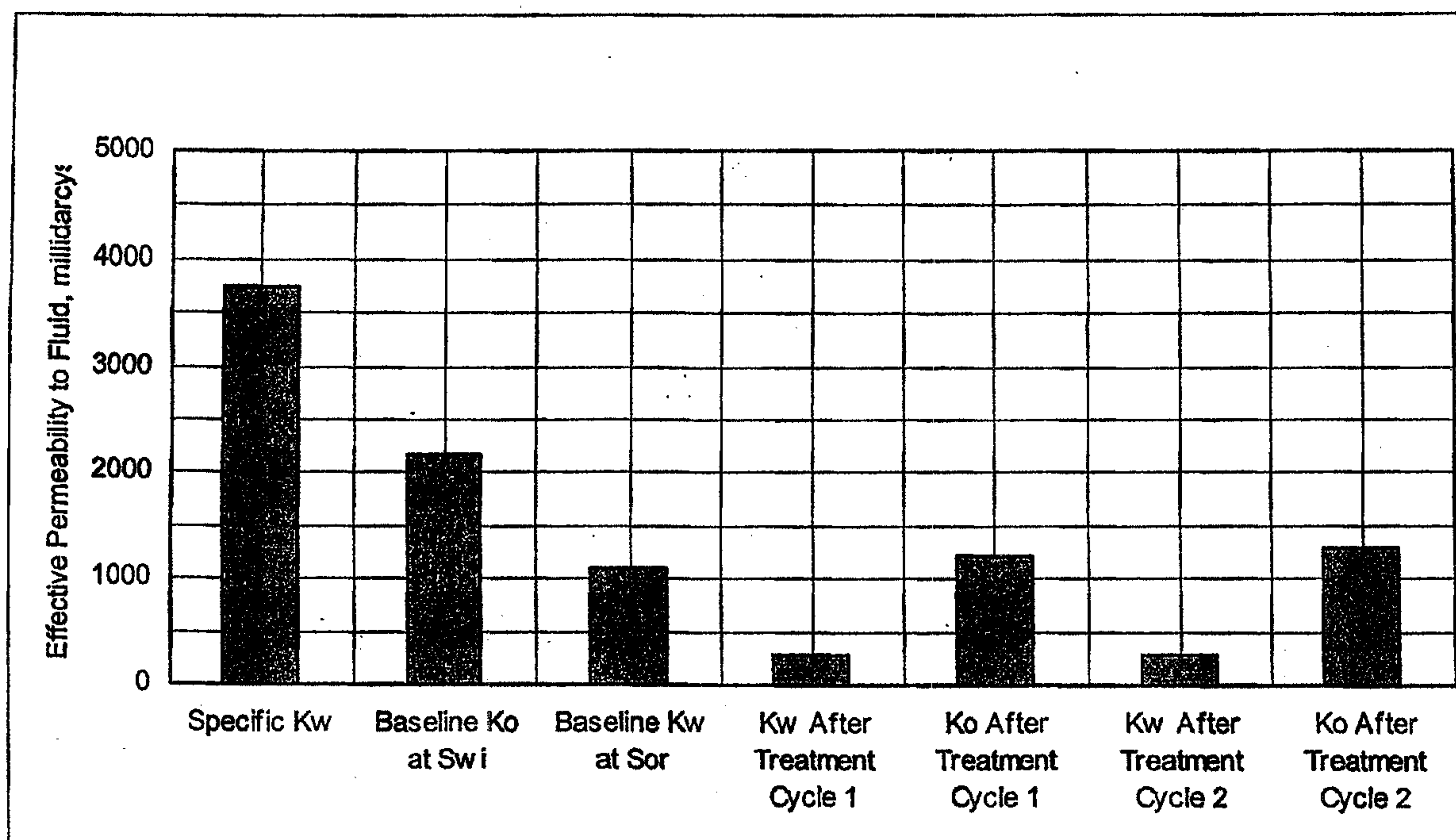


FIG. 2

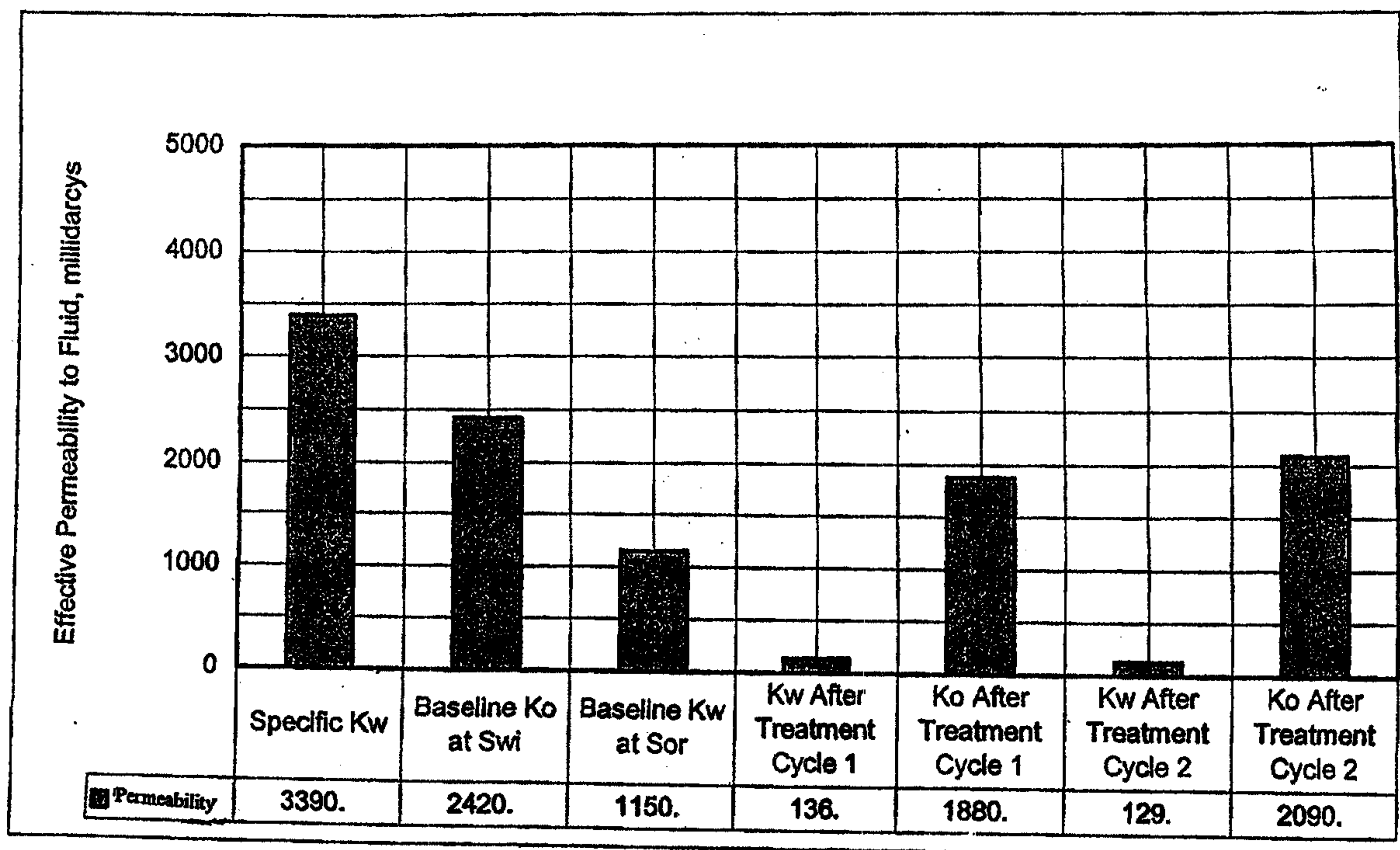


FIG. 3

