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3,136,360

METHODS USEFUL IN TREATING EARTH FORMATIONS

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No Drawing. Filed Apr. 25, 1960, Ser. No. 24,227
11 Claims. (Cl. 166—12)

This invention relates to the treating of earth formations to control the flow of fluid into and through pore spaces and other openings providing fluid passageways therein. More particularly, the invention relates to compositions and methods useful in sealing-off a permeable zone or section of an earth formation, such as a formation penetrated by the bore of an oil or gas well or the like, and further relates to controlling the injection of sealing or seal-forming compositions into the permeable formations to be treated.

The present application is a continuation-in-part of copending United States application Serial No. 711,153, which was filed on January 27, 1958, and is now abandoned.

It is anticipated that the invention will be applied most widely in connection with treating operations performed for the purpose of sealing-off earth formations into which it is relatively difficult to inject sealing compositions. One application wherein the invention provides particular advantages is in connection with the sealing-off of underground water-bearing formations in wells being drilled by the air or gas drilling method.

The technique of air or gas drilling differs from conventional drilling techniques mainly in that air or gas is used instead of a drilling liquid for the purpose of removing the cuttings from the bore hole. By the use of air or gas, the cuttings are discharged in the form of a dust or powder, rather than as part of a liquid stream.

As long as no water zones are encountered the air or gas drilling method has many advantages. However, it is very infrequent that water zones are not encountered. When the drill bit penetrates a water zone, the water flows into the bore hole with obvious disadvantages. The air or gas pressure is not sufficient to blow any appreciable quantities of water out of the bore hole. The water will wet the cuttings, which results in a sticky mass which cannot be blown out of the bore by the air or gas. In addition, the wetted cuttings tend to clog the drill bit and cling to the walls of the well bore. In many instances the drill bit and drill pipe becomes firmly stuck in the bore hole.

Since the advent of air and gas drilling, the undesirable production of water has been the major drawback to its universal application. As a result, extensive efforts have been devoted to the solution of the problem of shutting off the flow of water into the bore hole.

A suggested method for sealing a porous formation is described in United States Patent No. 2,801,984 to Morgan and Padbury, issued August 6, 1957. In accordance with this patent, a copolymer mixture is injected into the porous formation, and by reacting with the soil of the formation converts the composition in situ to a water-insoluble state, thus, sealing the porous formation. However, applicants' attempts to apply this method in shutting off flowing water were unsuccessful. It was discovered that a formation which produces water has entirely different characteristics from a non-producing porous formation which obviously will readily receive liquids. For example, in attempting to pump thickened liquids into a water producing zone, it was found that a fracture was inevitably created. In the oil well art it is well known that the creation of fractures increases production from the fractured zone. Therefore,

such fractures of a water-producing zone increase the water flow instead of reducing it.

Another major problem heretofore encountered has been the difficulty of controlling the time of gelation of the sealing composition used in treating an underground earth formation. It is desirable to avoid premature gelation, such as may occur while the composition is in the well conduit prior to reaching the formation to be treated. This occurrence has at times resulted in an unsuccessful operation which was time consuming and costly.

Even where the time of gelation may be successfully controlled, however, it has been found difficult in many instances to inject the sealing composition in sufficient quantities at the desired location and for the desired distance into the earth formation to obtain a successful shut-off of the water. This is particularly the case where the sealing composition contains colloidal or other particles which tend to clog the pore spaces and other openings in the formation and, in this way, reduce or obstruct the entry of the sealing composition into the formation in the required amounts.

A general object of the present invention is to provide improved compositions and methods useful in treating earth formations to control the flow of fluid in passageways therein.

Another object of the invention is to provide improved treating compositions for use in wells and to provide an improved well treating method wherein such compositions are utilized in sealing-off or substantially closing passageways in the underground strata penetrated by the bore of the well.

Another object of the invention is to provide an improved treating composition and an improved method utilizing the same in treating an underground water-bearing formation.

A further and more specific object of the invention is to provide an improved treating composition and an improved method utilizing the same in sealing-off an underground water-bearing formation penetrated by the bore of a well in which air or gas drilling operations are being performed.

In accordance with the invention, the foregoing and additional objects and advantages are attained by utilizing a fluid-treating composition having sealing or seal-forming properties and containing an additive in the form of a filter aid material which increases the fluid loss properties of the composition during the injection thereof into an earth formation, such as into an underground water-bearing formation penetrated by the bore of a well.

As used herein, the term "filter aid material" includes material in the form of finely divided, water inert solid particles having suitable surfaces, such as irregular and/or porous surfaces, which permit the particles to be accumulated into permeable deposits, such as into layers forming a permeable filter cake. Examples of materials which may be successfully employed are the synthetic calcium silicate compounds which are commercially available from Johns-Manville under the names "Micro-Cel A," "Micro-Cel B," "Micro-Cel C," and "Micro-Cel E." Other examples are the diatomaceous silica materials which are commercially available, for example, from Johns-Manville under the names "Filter-Cel," "Celite 512," "Hyflo Super-Cel," and "Celite 503," which are listed here in order of increasing average particle sizes.

In one way of proceeding, a treating composition in accordance with the invention is prepared by combining a filter aid material with one or more of the ingredients used in preparing a gel or gel-forming composition.

Examples of gels or gel-forming compositions which may be successfully employed are the sodium silicate gels. These may be employed in well treating operations in a

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"two-shot system," such as where sodium silicate solution and a gelling agent therefor are separately introduced into the well and then allowed to come together at a desired location in or opposite the formation to be treated. Alternatively, the sodium silicate gels may be employed in a "one-shot system," such as where an indirect or delayed acting gelling agent is included with the sodium silicate solution introduced into the well. See the co-pending United States application Serial No. 22,681 filed by Homer McLaughlin, Jr., one of the inventors herein.

In another way of proceeding, the treating composition is prepared by combining a filter aid material with a polymerizable mixture capable in time of forming a gelled mass.

The polymerizable mixture may, for example, be a mixture of 95% acrylamide and 5% N,N' methylene bisacrylamide, together with a suitable catalyst, such as ammonium persulphate, as taught in United States Patent No. 2,801,985 to Roth. This mixture is capable of gelling in water, such as after mixing with water in the permeable zone or formation to be treated. It is emphasized that the polymerizable mixture, which is employed in conjunction with other chemicals, results in a gelled mass after a period of time and no reliance is made upon any reaction of the materials with the soil in the formation. This mixture is placed opposite a formation which it is desired to seal off. The mixture penetrates such formation and then gels, thereby sealing off the formation. As taught in the Roth patent, a catalyst is required to cause a solution of acrylamide and N,N' methylene bisacrylamide in water to gel. However, such a solution has a corrosive effect on metallic substances. In turn, the products of corrosion will cause the solution to flash set. Thus, if such a solution is pumped down a metallic well conduit, a corrosion inhibitor should be included.

Another factor to be considered in using the acrylamide and N,N' methylene bisacrylamide solution, with the catalyst added, is the effect of the pH of the solution on the rate of gelation. At a very high or very low pH the gel time is indeterminate and the strength diminishes rapidly. Under these conditions, no control could be exercised in placing the solution in a well bore, as it might gel at any time. Therefore, a salt which will control the pH is required. The preferred pH of the solution is 8. However, a pH in the range of 7 to 12 has been found to be satisfactory.

Thus, a solution of acrylamide and N,N' methylene bisacrylamide, a catalyst, a corrosion inhibitor, and a salt to control the pH of the solution provide a composition which may be employed in shutting off a water producing formation. However, it has been discovered that temperature conditions affect the time of gelation, and indiscriminate mixing of the above substances results in a solution which is not controllable as to time of gelation or viscosity. In particular, it has been found that the dry ingredients should be added to the water in a prescribed sequence. In addition, different proportions are required for various temperature ranges.

Where this polymerizable mixture is employed, the following is the preferred sequence of steps to be followed, with continuous mixing of the ingredients:

(1) Add disodium phosphate duohydrate (DPD) to the water. This is a salt which controls the pH of the final solution.

(2) Add a polymerizable mixture comprising about 95% acrylamide and 5% N,N' methylene bisacrylamide. This is the basic gelling material.

(3) Add potassium ferricyanide (KF). This is the corrosion inhibitor to prevent flash setting.

(4) Add the filter aid material, such as a purified diatomaceous silica filter powder of medium size. This aids the final solution in penetrating the formation.

(5) Add a booster for the catalyst. Sodium thiosul-

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phate, commonly called Hypo, is an example of a suitable booster. The booster is only required at the lower temperatures.

(6) Finally, add the catalyst, such as ammonium persulphate (AP).

(7) Continue to mix the solution for approximately 5 minutes.

The resulting solution has a viscosity about the same as water and will not gel until the times shown in the table below elapse.

In order to compensate for the different temperature conditions, the percentages of materials in the table below should be used. However, some variations are permissible. In the following table a solution of acrylamide and N,N' methylene bisacrylamide in water is prepared by mixing 10 parts acrylamide and N,N' methylene with 90 parts of water, by weight, with 2 percent DPD added.

Temp. Range, ° F.	Hypo, percent	AP, percent	KF, percent	Gel Time, ¹ Low Temp., min.	Gel Time, ¹ High Temp., min.
65-90	0.5	1.0	0.02	87	45
90-120	0.5	0.5	0.04	88	52
120-140	None	0.5	0.04	95	48
140-150	None	0.2	0.08	105	75
150-160	None	0.2	0.12	107	64
160-180	None	0.2	0.16	105	43
180-200	None	0.2	0.18	53	40

¹ Actual pumping or grouting time.

In yet another way of proceeding, also in accordance with the invention, the treating composition is prepared by combining a filter aid material with one or more of the ingredients used in preparing a chrome lignin gel.

For example, the treating composition may be a chrome lignin gel prepared by combining 120 grams of lignin liquor (clarion extract), 96 milliliters of water and 5.2 grams of chromic acid, with the filter aid material being added to one or more of the ingredients and, in any event, being preferably uniformly dispersed in the final mixture.

Laboratory tests have been conducted for the purpose of comparing the fluid loss properties of chrome lignin gels, which were prepared as aforesaid and to which varying amounts of filter aid materials were added. For these tests, a Baroid filter press was employed and the measurements were made following generally the procedure of the API code for testing drilling muds. The results of these tests are shown in Table I.

Table I

Sample No.	Filter Aid	Amount grams	Fluid Loss
1	None	None	53 ml.—30 min.
2	Micro-Cel C	10	319 ml.—30 min.
3	do	5	410 ml.—30 min.
4	do	2.5	528 ml.—29.5 min.
5	do	2	550 ml.—24 min.
6	do	1.5	490 ml.—30 min.
7	do	1	330 ml.—30 min.
8	Micro-Cel B	2	552 ml.—30 min.
9	Micro-Cel E	2	293 ml.—30 min.
10	Micro-Cel A	2	540 ml.—7.5 min.
11	do	2	558 ml.—10.5 min.
12	do	1.5	558 ml.—18.6 min.
13	do	1	372 ml.—30 min.
14	Filter-Cel	1	160 ml.—30 min.
15	Celite 512	1	385 ml.—1.75 min.
16	do	1.5	580 ml.—3.1 min.
17	Hyflo Super-Cel	0.75	582 ml.—12.1 min.
18	do	1	370 ml.—1 min.
19	do	1.5	550 ml.—2.3 min.
20	do	3	580 ml.—1.67 min.
21	Celite 503	1	370 ml.—4.25 min.
22	do	1.5	336 ml.—30 min.

In order to treat a water producing formation in a bore hole drilled by the air or gas method, the proper ingredients for the temperature condition existing at the formation are selected. The treating solution is prepared, such as by following one of the procedures outlined above, and then the solution is placed opposite the formation by any

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of the several methods which are well known in the art. Sufficient pressure is exerted on the treating fluid to inject it in the formation. Care must be exercised to prevent the application of too much pressure or the formation will be fractured.

After the formation accepts a sufficient amount of treating fluid and the gelation has occurred in the formation, at least 30 minutes should elapse before continuing drilling operations. Any gelled material in the tubing or drill pipe can easily be removed by pumping. The gelled material in the formation seals the water producing pores and is of sufficient strength to hold back the water behind the gelled seal.

It should be readily apparent that applicant has devised a novel composition of matter adapted to shut off the production of water in a bore hole drilled by the air or gas method.

The use of the novel composition is not limited to shutting off water as described above. It will be readily apparent to those skilled in the art that the material can be injected into any porous formation or into fissures and thereby seal off the same. It is also apparent that equivalent materials, methods, and applications may be employed without departing from the spirit of the invention and the appended claims.

What is claimed is:

1. In a method of treating an earth formation with a treating composition containing gel-forming constituents selected from the group consisting of water-soluble polymerizable materials and chrome lignin materials, the step of adding to said composition a finely divided water inert filter aid material in sufficient quantity to substantially increase the fluid loss of said composition into the formation to be treated.

2. The invention as claimed in claim 1 wherein said treating composition is a gel-forming composition consisting essentially of a sodium silicate solution, and a gelling agent for said solution.

3. The invention as claimed in claim 1 wherein said treating composition is a gel-forming composition consisting essentially of lignin liquor and chromic acid.

4. The invention as claimed in claim 1 wherein said treating composition is a treating fluid having a pH in the range of 7 to 12, the essential ingredients of said fluid being a solution in water of a polymerizable mixture comprising about 95% acrylamide and 5% N,N'-methylenebisacrylamide and a catalyst.

5. The method of sealing off an underground formation penetrated by the bore of a well which comprises the

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steps of introducing into the well bore a gel-forming composition containing a finely divided, water inert filter aid material in sufficient quantity to substantially increase the fluid loss of the composition into the formation; placing the composition opposite the formation to be sealed off; exerting sufficient pressure to inject at least a portion of the composition into said formation; and maintaining pressure on the composition until gelation thereof occurs in said formation.

6. The invention as claimed in claim 5 including the step of forming a permeable filter cake of said filter aid material on said well bore as said composition is injected into said formation.

7. The method of claim 5, wherein said gel-forming composition comprises a dispersion of a chrome lignin material.

8. The method of claim 5, wherein said gel-forming composition comprises a sodium silicate material.

9. The method of claim 5, wherein said gel-forming composition comprises a water soluble polymerizable mixture.

10. The method of sealing off an underground formation penetrated by the bore of a well, which comprises the steps of introducing into the well bore an aqueous treating composition containing gel-forming constituents and containing a finely divided, water inert filter aid material in sufficient quantity to substantially increase the fluid loss of the composition into the formation; placing the composition opposite the formation to be sealed off; exerting sufficient pressure to inject at least a portion of the composition into said formation; and maintaining pressure on the composition until gelation thereof occurs in said formation.

11. The method as defined in claim 5, wherein said gel-forming constituents comprise a water soluble polymerizable mixture, and including the step of forming a permeable filter cake of said filter aid material on said well bore as said composition is injected into said formation.

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