United States Patent Office

Б

2,778,427 Patented Jan. 22, 1957

2,778,427

ACIDIZING WELLS

1

Paul H. Cardwell and Parke D. Muir, Tulsa, Okla., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

No Drawing. Application February 18, 1952, Serial No. 272,266

4 Claims. (Cl. 166-42)

The invention relates to acidizing wells drilled into the 15 earth. It more particularly concerns an improved hydrochloric acid composition for acidizing wells and method of increasing the output of oil and gas wells by the injection into the contiguous earth of an aqueous solution containing hydrochloric acid. 20

In the usual well acidizing operation, as for the purpose of increasing the output of a well, the hydrochloric solution with or without fortification with a soluble fluoride is introduced into the well, and, when sufficient pressure is available or supplied, and the formation is sufficiently 25 permeable, the acid also enters the adjacent earth formation. Acid-soluble matter of the earth contacted by the acid is attacked and dissolved away, thereby increasing the size of the well hole and enlarging the interstices of the adjacent formation through which the earth fluids 30reach the well. In some cases, sufficient pressure may be applied to the acid solution in the well hole to cause the acid to fracture and lift the overlying earth adjacent to the well, thereby forming passageways in the earth by hy-35 draulic action and subjecting them to the solvent action of the acid. Essentially the same acidizing operations are performed in increasing the receptiveness of injection wells. The effectiveness of the conventional acidizing operation to increase the productiveness of a well (or to increase the receptivity of an injection well for fluid), we have found, appears to depend at least in part upon the nature of the solvent action of the acid. According to our investigations, including numerous tests on cores taken from calcareous formations, the conventional hydrochloric acid solution used in well acidization, when forced into and through a more or less fluid permeable core comprising acid-soluble matter, attacks the core mostly at the face exposed to the acid solution and rapidly dissolves it away. At the same time, some of the 50acid permeates the innumerable interconnected pores or interstitial spaces in the body of the core and becomes spent therein, thereby more or less increasing the flow capacity of the core. The resulting increased capacity for fluid flow, under a given pressure head, is not as great 55 as it would be, if, instead of either enlarging each of the innumerable pores of the interstitial space or attacking the face of the formation, as in conventional acidizing, the acid were to expend itself in only a few of the existing pores so as to form a few large passageways from the well 60 hole deeply into the earth formation. In addition, by forming fewer but larger passageways, and not expending itself either on the face of the formation or throughout the interstitial spaces therein, a smaller quantity of acid would suffice to form passages reaching farther into the 65 formation before becoming spent. It is a desideratum of the art to overcome the shortcomings of conventional acidizing and to achieve greater effectiveness of the action of the acidizing solution.

It is, therefore, an object of the invention to provide 70 an improved acid composition for and method of acidizing wells in which the tendency for the acid to become in2

effectively expended in attacking the wall of the well hole as well as becoming ineffectively dissipated in multitudes of interconnected pores in the adjacent formation is overcome, if not substantially reduced. Other objects and advantages will become apparent as the description of the invention proceeds.

The invention is predicated upon the discovery that by including in the hydrochloric acid solution, which is injected into the earth formation adjacent to the well in 10 the acidizing operation, between about 0.65 and 1.6 percent by weight of certain water-soluble cellulose ethers which at least temporarily thicken or increase the viscosity of the acid solution and deposit a water absorbent gel-like film or coating on the surface of the earth formation to be acidized, the hydrochloric acid solution no longer permeates the entire interstitial space in the earth formation into which the solution is injected, but instead becomes selective in its action in that it permeates the earth formation only in a comparatively few places per 20 unit of area of the earth formation exposed to the acid solution in the well hole. The acid solution containing the water-soluble cellulose ether in accordance with the invention, has the peculiar property of entering and greatly enlarging only a few of the pores in the earth formation being acidized. The pores thus enlarged become passageways which have the appearance of "worm holes" and have a more or less uniform diameter, the diameter of most of them being between about 0.05 and 0.3 inch. These worm holes extend from the face of the well hole through which the acid enters the formation and penetrate deeply into the formation, and the face of the formation through which the acid passes into the formation is but slightly eaten away. The passageways thus formed are usually branched. Sometimes one or more branches form from a single passageway entering the face of the formation and sometimes two or more passageways, entering the face of the formation, will combine into a single passageway as the passageways lengthen. While the formation becomes thus acidized, the acid decomposes more or less of the cellulose ether, and, as the acid becomes fully spent in the passageways or worm holes so made, more or less undecomposed cellulose ether may remain as a deposit on the walls of the worm holes. Nevertheless, as a result of the acidizing, the fluid permeability of the formation is greatly increased. If desired, hydrochloric acid solution free from cellulose ether may be injected into the formation after or behind the cellulose ether-containing acid to assist in decomposing in the formation deposits of cellulose ether which might tend to reduce the flow capacity of the worm holes. Examples of water-soluble cellulose ethers which produce these desirable effects in hydrochloric acid solution containing from 2 to 25 percent of HCl are water-soluble alkyl cellulose ethers, the water-soluble carboxyalkyl cellulose ethers, and the hydroxy alkyl cellulose ethers. Examples of such ethers are: methyl cellulose, ethyl cellulose, carboxymethyl cellulose, carboxyethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, methyl carboxymethyl cellulose, ethyl carboxymethyl celluose, methylethyl cellulose, and hydroxy propylmethyl cellulose.

It has been further discovered that by increasing the viscosity of the hydrochloric acid solution to a comparatively high range of viscosity, e. g. 1000 cps. to 51,000 cps., by using at least one of the aforesaid cellulose ethers in amount exceeding about 1.6 percent but not more than about 4 percent, and applying very high pressures to the so-thickened acid solution, i. e. pressures exceeding the weight per unit area of the overburden of earth above the formation being acidized, a hydraulic jacking action is readily obtained without either excessive penetration into or wastage of the acid in the interstitial space. Upon

5

35

6

releasing the pressure after the injection, the formation is left deeply channelled and fractured and in a condition either to produce or receive fluid more readily.

Undecomposed cellulose ether remaining in the formation after an injection of the cellulose ether-containing acid solution may be decomposed by introducing into the formation a charge of hydrochloric acid free from the cellulose ether as aforesaid. For this purpose, there may be used a volume of cellulose ether-free hydrochloric acid (containing 2 to 25 percent of HCl) which is from 1 to 10 25 times the volume of the cellulose ether-containing acid used. A preferable amount to use is about 6 volumes of cellulose ether-free acid for each volume of cellulose ether-containing acid with cellulose ether concentrations of 0.65 to 1.6 percent; and preferably about 2 volumes of cellulose ether-free acid for each volume of cellulose ether-containing acid when the concentration of the cellulose ether exceeds about 1.6 percent. In formations which are largely sand or acid-insoluble, the cellulose ether generally decomposes in due time before the acid becomes spent without the need for an injection of cellulose ether-free acid behind the cellulose ether-containing acid.

In treating a well in accordance with the invention, an aqueous hydrochloric acid is used, such as one containing from about 2 to 25 percent of HCl by weight. In most instances, a concentration of about 10 to 15 percent of HCl by weight is generally suitable. The acid solution is more or less thickened in accordance with the invention by mixing therewith, before its introduction into the earth formation, the desired amount of the water-soluble cellulose ether. These cellulose ethers are comminuted solids and may be mixed with the acid solution in any suitable manner as by vigorously agitating the acid solution while slowly adding the requisite amount of the cellulose ether to produce the desired increase in viscosity but not beyond a pumpable viscosity. A preferable method of thickening the acid solution is first to suspend the cellulose ether in an aqueous solution of a water-soluble inorganic salt, such as a solution of sodium chloride in water, the salt having a concentration sufficient to prevent substantial swelling of the cellulose ether while allowing the cellulose ether to be wetted by the solution. Thereafter, the suspension of the cellulose ether in the salt solution is mixed with the hydrochloric acid solution to produce the desired thickening. Various salts in various concentrations may be so used. The rate of swelling increases as the concentration of the salt decreases. In high concentrations, the salt will be precipitated when the mixture is added to the hydrochloric acid solution and the higher concentrations of salt also tend to prevent the cellulose ether from thickening the acid solution. The lower concentrations of salt allow rapid thickening to Concentrations of salt between these extremes occur. preferably are used, if at all, as for example, in the case of sodium chloride, from 0.7 to 2.2 pounds of NaCl per gallon of water. Suitable concentrations of other salts may be determined by trial.

The cellulose ether-salt water mixture is, as aforesaid, added to the hydrochloric acid solution, the proportions being determined by the amount of thickening desired of the acid solution. It is to be understood that the use of the salt water dispension procedure for introducing the cellulose ether into the acid solution is not essential, although its use is preferable as it obviates the tendency for 6 the cellulose ether to form difficultly dispersible lumps when the cellulose ether is added directly to the acid sclution unless slowly added with vigorous agitation. When the salt solution containing the cellulose ether is mixed with the hydrochloric acid solution, there should be suf- 7 ficient water present in either the salt solution or the acid solution or both solutions to dilute the salt to a concenration below that in which the salt does not substantially interfere with the thickening action of the cellulose ether on the resulting acid mixture produced. In the case of 75

sodium chloride, for example, as much as 0.5 pound of NaCl per gallon of the resulting mixture, comprising the aqueous hydrochloric acid solution and cellulose ether, may be tolerated without substantial effect by the salt on the thickening action of the cellulose ether.

4

The data in Table I is illustrative of the thickening effect of various amounts of a celluose ether on a hydrochloric acid solution containing from 5 to 15 percent of HCl at two temperatures, the solution being formed by adding a dispersion of the cellulose ether in salt water to the hydrochloric acid solution.

15	Pounds of cellulose ether ¹ per 1,000 gal- lons of hydrochloric acid solution (5 to 15% HCl)	Viscosity in centipoises of acid solution containing cellulose other			
		80° F.	120° F.		
20	60 81 90 150	100 170 210 900	100 125 540 9 250		
25	210247 247	3,900 10,000 16,800 51,000	2, 350 6, 050 10, 000 31, 000		

 1 Hydroxy propylmethyl cellulose having a viscosity of 4,000 cps. in 2% aqueous solution.

Other cellulose ethers may be used in similar proportions with approximately the same effect on the viscos-30 ity of the hydrochloric acid solution. For example, the amounts of cellulose ether required to prepare a 5 to 15 percent HCl solution having a viscosity of 10,000 cps. at various other temperatures are shown in Table II.

TABLE II

	Pounds of cellulose ether per 1,000 gallons of hydrochloric acid solution (5–15% HCl)	Tempera- turc, ° F.
40	244 251	70
	255 261	100 110

As soon as the thickened aqueous mixture of the hydrochloric acid and the cellulose ether is prepared, its vis-45 cosity gradually declines, the rate of decline being greater the higher the HCl concentration and temperature. Data are set forth in Table III showing the viscosity, after various elapsed times, of hydrochloric acid solution of 50various HCl concentrations at several temperatures, each mixture containing enough cellolose ether to initially provide a viscosity of 10,000 cps.

TABLE III

	HCl Content,	Elapsed Time,	d Viscosity in Cps. at-							
Percent	Min.	70° F.	80° F.	90° F.	100° F.	110° F.	120° F			
1	5	30	9, 750	8, 850	8, 400	7, 250	6, 050	3, 55		
ł	7.5	30	8, 850	8,350	7,850	6, 550	5,160	3, 20		
	10	30	8,000	7,400	6,350	4,450	3, 350	2, 4		
	12.5	30	7,200	6,300	5,150	2,700	1,350	30		
	15	30	6, 500	4, 500	3,100	1, 425	<200	<20		
ł	5	60	9, 550	7,900	7,100	5, 350	3, 670	1, 3		
,	7.5	60	7,900	7,050	6,200	4, 350	2, 670	6		
1	10	60	6, 300	5,600	4,000	2,070	1, 120	< 2		
1	12.5	60	5,150	4,100	2,730	780	<200	< 2		
1	15	60	4, 100	2,000	990	220	<200	<2		
	5	120	9, 150	6, 300	5, 000	2, 950	1, 375	$ <^{2}$		
1	7.5	120	6, 270	5,000	3, 850	1, 950	710	< 2		
1	10	120	3, 970	3, 150	1,670	456	<200	<2		
	12.5	120	2,600	1,700	785	<200	<200	<2		
	15	120	1,600	400	200	<200	<200	$ <^{2}$		
	5	240	8, 450	4,000	2, 520	890	<200	$ <^{2}$		
	7.5	240	4,000	2, 460	1,470	392	<200	$ <^{2}$		
	10	240	1, 550	990	295	<200	<200	<2		
	12.5	240	690	295	200	<200	<200	$ \leq 2$		
ł	5	360	7, 700	2, 530	1,260	<200	<200	< 2		
1	7.5	360	2, 520	1,230	562	<200	<200	$ <^{2}$		

In Tables II and III, each of the thickened hydro-

chloric acid solutions had an initial viscosity of 10,000 cps. which is obtained by including in the acid solution various amounts of cellulose ether. In 1000 gallon batches, these thickened hydrochloric acid solutions are prepared as follows: salt (NaCl) is dissolved in water in the proportions of 480 pounds of NaCl to 220 gallons of water. If desired, a surface tension lowering agent may be added, e. g. a liquid petroleum sulfonate, and then the required amount of cellulose ether is stirred into the salt solution. The amount of cellulose ether used 10 is determined from Table I (although other amounts may be used according to the viscosity desired in the thickened acid solution and the temperature at which the thickened acid is to be used). For use at 80° F., for example, as in making 1000 gallon batches of thickened hydrochloric 15 acid, which correspond to the thickened acid solutions

The following tests, the data of which are tabulated in Table V, are illustrative of the worm-hole forming action of the cellulose ether-thickened acid of the invention on calcareous formations. Cylindrical cores 1 inch in diameter and 1 inch long were cut from Bedford limestone and used in the tests. Before acidizing, the cores had an average permeability of 50 millidarcys and allowed the passage from end to end of the core of 0.05 cc. of oil (2 cps. viscosity) per minute at a pressure of 1 pound per square inch. In the acidization, 50 cc. of hydrochloric acid solution at various temperatures and containing various amounts of HCl and cellulose ether (hydroxypropyl methyl cellulose), as noted in the table, were applied to each core under 60 pounds pressure per square inch from one end, the other being open to the atmosphere.

TABLE V

Core No.	Acidiz- ing Temp.,	Percent HCl in Solution	Lbs. hy- droxy pro- pyl methyl	Number of through channels formed in core		Average channel diameter,	Average length of core after acidizing.	Amount of Acid Neu- tralized during	Permeability of core after acidizing cc. oil ² per min.	Dura- tion of acidiz- ing.	
1	° F.	F. cellulose		Inlets	Outlets	inch		inches	acidizing, milliliter	at 1 lb. pres- sure	mins.
1 2 3 4 6 7	80 80 100 100 100 120	15 15 15 10 10 10 5	none 50 100 none 50 100 none	none 2 2 none 3 1 none	none 4 1 none 2 3 none	0. 14 0. 09 0. 16 0. 11	2332 3132 3132 1316 3132 3132 3132 3142 3142 3142 3142 3142	30 8 2 50 10 5 48	0. 10 880 192 0. 06 990 352 0. 06	15 12 14 15 11 13 15	
8 9	120 120	5 5	50 100		$2 \\ 2$	0.20 0.12	81/32 31/32	33 8	1285 484	10 14	

¹ Per 1,000 gallons of the HCl solution. ² 2 cps. viscosity.

having the viscosities set forth in the fourth column of Table III, about 247 pounds of cellulose ether is used. ³⁵ This may be in the form of hydroxy propylmethyl cellulose (having a viscosity of 4000 cps. when dissolved in water in a concentration of 2 percent by weight), as shown in Table I. For making a similar batch of acid usable at 120° F., for example, the amount of cellulose ether to produce the thickened hydrochloric acid solutions having viscosities set forth in the last column of Table III is 268 pounds. Amounts of the same cellulose ether for use at other temperatures are shown in Table II.

After mixing the selected amount of cellulose ether ⁴⁵ with the aforesaid salt water solution so as to thoroughly wet the cellulose ether with the salt water solution, the resulting dispersion is added to 750 gallons of aqueous hydrochloric acid having a higher HCl concentration than that desired finally in the thickened acid. The higher concentration of HCl is chosen so as to compensate for the dilution effect of the added salt water solution containing the cellulose ether. In Table IV is set forth the approximate concentration of HCl to have present in the 750 gallons of aqueous hydrochloric acid solution so that upon dilution with the salt water dispersion of the cellulose ether the resulting acid solution will have the HCl concentrations corresponding to those of the thickened hydrochloric acid solutions of Table IV.

TABLE IV

Percent of HCl by weight in hydro- chloric acid before add.tion of cellu- lose ether-salt wa- ter dispersion. Vol- ume of solution 750 gallons	Percent of HCl by weight in the thick- ened hydrochloric acid solution result ing from addition of cellulose ether- salt water disper- sion. Volume of solution 1,000 gal- lons	
7 10 13 16, 5 20	57.51012.515	

Referring to Table V, it is to be noted that prior to acidizing there were no passages or worm holes in the cores evident to the naked eye. Each core was sound before as well as after acidizing with the cellulose ethercontaining acid. As a result of the acidizing with the cellulose ether containing hydrochloric acid solution, each of the cores were traversed from end to end with one or more passageways or channels (elsewhere referred to as worm holes) as enumerated in the table. From end to end, most of the passages were more or less crooked and branched but invariably led away from the end of the core through which the acid solution entered and proceeded in a direction more or less parallel to the direction of maximum initial permeability. It will be observed also that a number of advantageous effects is obtained by virtue of the addition of the cellulose ether to the acid solution. Referring to cores 1, 2 and 3, for instance, it will be noted that the acid solutions at 80° F. containing 50 and 100 pounds of hydroxypropyl methyl cellulose per 1000 gallons respectively dissolve away only about 1/32 inch of the end of the core which is exposed to the acid solution while at the same time large passageways are formed all the way through the cores but 16 percent and 4 percent respectively of the acid becomes neutralized. The passageways formed exhibit from 17600 (core #2) to 3840 (core #3) times the original flow capacity of the cores for oil. In further comparison 60 under similar test conditions, conventional cellulose etherfree hydrochloride acid dissolves away more than 28 percent of the core (#1) and 60 percent of the available acid becomes neutralized without forming any channels, and only doubles the flow capacity of the core for oil. 65 Similar passageway or channel formation and increases in flow capacity with low HCl consumption are obtained with cellulose ether-containing acid similarly used at 100° F. and 120° F., as shown in the Table V, while conventional cellulose ether-free hydrochloric acid solution under 70 similar acidizing conditions increases the flow capacity only about 20 percent with a consumption of 96 percent or more of the acid.

A corrosion inhibitor may be included in the cellulose ether thickened acid solution to protect the metal parts 75 of the well from attack by the acid. In addition, there

may be included an emulsion breaking agent to prevent the possibility of the thickened acid solution from forming undesirable emulsions with oil in the oil-producing formations.

The following examples are illustrative of the practice of the invention in acidizing oil wells.

Example 1

A well was drilled into the Arbuckle lime formation in the silica pool in Kansas to a depth of 3271 feet. The well was provided with the usual casing and tubing. The producing formation was at about 115° F. Before treating according to the invention, the well produced 37 barrels of oil and 23 barrels of water per day.

A salt solution was made by dissolving 265 pounds of 15 sodium chloride in 165 gallons of water in a truck tank. About 2 gallons of a wetting agent comprising a petroleum sulfonate was mixed with the resulting salt solution and then 165 pounds of methyl cellulose (having a viscosity of 4000 cps. in 2 percent water solution) was dispersed in the solution.

In another truck tank, 562 gallons of aqueous hydrochloric solution containing 13 percent of HCl by weight was mixed with 3 gallons of a corrosion inhibitor and 3.75 gallons of an emulsion breaking agent.

The truck tanks containing the above mixtures were brought to the well site. A packer was run on the tubing string, the well is filled with oil and then the packer was set just above the producing formation. Oil was then pumped through the tubing string into the formation at 30 the rate of 10 gallons per minute which required a pressure at the head of the tubing string of 1400 pounds per square inch.

The mixtures were withdrawn from each of the truck tanks in continuous streams in the ratio of 3 volumes of the hydrochloric acid mixture to 1 volume of the cellulose ether mixture, the streams being brought together and mixed and the mixture continuously injected into the well through the tubing. The viscosity of so-prepared mixture was 4000 cps. As the mixture reached and entered the producing formation, the injection pressure measured at the head of the tubing string increased to 3900 pounds per square inch and then declined to 2200 pounds per square inch in 16 minutes when all the mixture has been injected into the well. 2.25 hours after the injection the pressure was released and the solution then withdrawn from the well had a viscosity of 40 cps. Following the treatment, the well produced 92 barrels of oil and 39 barrels of water per day.

Example 2

A well was drilled in the Gorham sand in the Gorham pool in Kansas to a depth of 3404 feet. The well was provided with the usual casing and tubing. The tem-perature of the producing formation was 115° F. Before 55 being acidized according to the invention, the well's daily production rate was 7 barrels of oil and 11 barrels of water.

A salt solution was made by dissolving 350 pounds of NaCl in 220 gallons of water in a truck tank and 1.5 gallons of a petroleum sulfonate wetting agent was mixed with the resulting solution. Into the salt solution was stirred 220 pounds of methyl cellulose (having a viscosity of 4000 cps., in 2 percent aqueous solution) until wetted by and dispersed in the salt solution.

In another truck tank were mixed together 750 gallons of a 13 percent HCl solution, 4 gallons of a corrosion inhibitor, and 5 gallons of an emulsion breaking agent.

The two truck tanks with the mixtures in them were brought to the well and a retainer was on the tubing in the well just above the producing formation. The well was then filled with water and the retainer set. Water was pumped into the formation through the tubing at the rate of 3 gallons per minute which required a pressure of 1700 pounds per square inch at the tubing head. 75 HCl by weight and thickened by having in admixture

The mixtures were withdrawn from each truck tank in continuous streams in the ratio of 3 volumes of the mixture containing the hydrochloric acid to 1 volume of the mixture containing the cellulose ether and mixed together continuously while injecting the so-prepared mixture into 5 the well. The mixture had a viscosity of 4000 cps. and contained 10 percent of HCl by weight. As the mixture entered the formation, the injection pressure measured at the tubing head reached 4500 pounds per square inch and declined to 3000 pounds per square inch in 20 10 minutes when the mixture was all in the formation. 2.25 hours after the injection, the pressure was released and the well allowed to produce. It delivered oil at the rate of 120 barrels per day with but a trace of water.

Although in the foregoing well-treating examples, the volume of the salt water suspension of cellulose ether is about 1/3 that of the hydrochloric acid solution, it is to be understood that other proportions may be used such as 1/5 to 1/2 (or none as already explained) but a 20water-soluble salt concentration of about 0.5 pound per gallon of the thickened acid solution preferably should not be exceeded. It is to be observed also that on raising sufficiently the temperature of the hydrochloric acid solution, thickened by the cellulose ether, gellifying occurs

25 of the cellulose ether which prevents the solution from pouring and it becomes unpumpable. The cellulose ether-thickened acid solution is used at temperatures below those which cause gelling to the extent of rendering the solution non-flowing or unpumpable. The gel-

ling temperature of cellulose ethers varies somewhat among the different ones and is usually not over about 130° F. The acid solution thickened with cellulose ether is injected into the earth formation at a temperature below that causing gelling, e. g. 125° F. 35

The worm hole forming action already referred to in which the acid solution produces worm hole-like passages through or into the earth formation, appears to reach a maximum with amounts of cellulose ether providing an initial viscosity of about 300 cps. To obtain this viscosity requires about 100 pounds of cellulose ether per 1000 gallons of acid solution, although amounts as high

as those producing a viscosity of 1000 cps. may be used, such as about 135 pounds of the cellulose ether per 1000 gallons of the acid solution. For lifting the

overburden as when very high injection pressures are used, the acid solution preferably contains from about 150 to 315 pounds of cellulose ether per 1000 gallons of the acid solution.

As already indicated in the examples, a corrosion in-50hibitor may be included in the thickened acid solution to protect the metal parts of the well from attack by the acid. In addition, there may be included an emulsion breaking agent to prevent the possibility of the thickened acid solution from forming undesirable emulsions with oil in the oil-producing formations.

This application is a continuation-in-part of our copending application Serial No. 213,048, filed February 27, 1951, now abandoned.

We claim:

60

1. In a method of acidizing an earth formation penetrated by the bore of a well the steps which consist in injecting into the earth formation through the well bore an aqueous solution containing from 2 to 25 percent by weight of HCl and having dispersed therein from 0.65

65 to 4 percent by weight of a water-soluble cellulose ether, and thereafter injecting into the earth formation between 1 and 25 times as much in volume of an aqueous solution containing from 2 to 25 percent of HCl by weight $_{70}$ free from cellulose ether.

2. In a method of acidizing an earth formation penetrated by the bore of a well, the steps which consist in injecting into the earth formation through the well bore an aqueous solution containing from 2 to 25 percent of

therewith from 150 to 315 pounds of a water-soluble cellulose ether per 1000 gallons of the said aqueous solution, and raising the pressure on the said thickened aqueous solution in the well hole to an amount exceeding that per unit area of the overburden of earth.

per unit area of the overburden of earth. 5 3. In a method of acidizing an earth formation penetrated by the bore of a well, the steps which consist in injecting into the earth formation through the well bore an aqueous solution containing from 2 to 25 percent of HCl by weight and thickened by having in admixture 10 therewith from 150 to 315 pounds of a water-soluble cellulose ether per 1000 gallons of the said aqueous solution, raising the pressure on the said thickened aqueous solution in the well hole to an amount exceeding that per unit area of the overburden of earth, and injecting into the well and thence into the formation an aqueous solution containing from 2 to 25 percent of HCl free from cellulose ether, the volume of the aqueous solution free from cellulose ether being from 1 to 25 times the volume of the aqueous solution containing the cellulose ether. 20

P

4. In a method of acidizing an earth formation penetrated by a well bore the step which consists in injecting into the earth formation through the well bore an aqueous solution containing from 2 to 25 percent by weight of hydrochloric acid and a water-soluble cellulose ether dispersed therein in amount from 100 to 315 pounds per 1000 gallons of solution.

References Cited in the file of this patent

UNITED STATES PATENTS

	2,265,914	Lilienfeld Dec. 9, 1941	
	2,316,745	Robertson et al Apr. 13, 1943	
	2,596,137	Fast May 13, 1952	
5	2,689,009	Brainerd et al Sept. 14, 1954	
	2,689,230	Cardwell et al Sept. 14, 1954	

OTHER REFERENCES

Frydlender: La Methy Cellulose, Article in La Revue 20 des Produits Chimiques, vol. XLII, No. 7, pages 193-198.