

## UNITED STATES PATENT OFFICE

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## METHOD OF TREATING WELLS

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This invention relates to methods of treating wells; and it comprises a method of treating oil wells which penetrate ground formations containing oil or gas and flowing water, for the purpose of selectively shutting off water inflow to the well without materially interfering with oil inflow, wherein there is introduced into the well and formation a solution of a cellulose derivative which on intermingling with water in the formation, deposits out an insoluble, bulky, sealing precipitate; all as more fully hereinafter set forth and as claimed.

Oil wells often pass through a variety of ground formations including oil bearing and water bearing formations, these often being closely adjacent. It is a desideratum to shut off the inflow of connate water or brine from wet formations and it is, of course, essential to avoid any stopping off of inflow of oil from the oil containing formations. No good way of effecting such selective stopping off has been known in the art. It is common practice to stop off all inflow to a well by means of mud or concrete plastering the walls. A frequent expedient is to inject a concrete mixture setting to a solid mass and later drill through the solid body thus formed. This expedient can be used for shutting off water occurring in the well bottom but it is not adapted for shutting off water occurring elsewhere than in the well bottom. In certain cases water formations lying above the oil formation can be shut off by steel casings. But this method is not discriminatory, is not effective in some situations and is always costly.

In an oil well there is a sharp pressure gradient at the well face and it is difficult to keep sealing materials in place at this point; the pressure behind tends to break the seal and clear the pores. The farther back in the formation the sealing material can be used in plugging pores, the better; the less is the difficulty in keeping it in place. The pressure gradient is not so high in points remote from the well face.

We have found a way to effect selective stopping off of water bearing strata, sealing them at points remote from the well face. We do this with the aid of certain organic colloidal solutions and suspensions of one kind or another. The solution used is one which precipitates on dilution or deposits by other ways, such as flocculation, a sealing plug or deposit in the water formation. Cellulose solutions, aqueous and non-aqueous, are especially useful for our purposes. The solution is forced into the well under pressure sufficient to drive it far back into the water

strata. Diffusion and intermingling of the solution with the water in the formation bring about the deposition desired. The solution is left in the formation, pressure being maintained, long enough for the deposition to take place. Ordinarily, deposition or precipitation does not take place immediately, but in the course of some minutes or hours. This delayed action insures against premature deposition.

In some cases, before injection of the treating solution, the well is first cleared of any brine or water standing therein by displacing the brine upwards with oil.

Little penetration occurs in the oil-containing strata, particularly in the case of aqueous solutions or suspensions; these being incompatible with oil. Moreover, the delayed actions utilized are generally of such character as not to occur in the absence of water or salines.

While solutions of various kinds of organic colloids having the properties described can be used, we have found that solutions of cellulose derivatives have particularly useful properties for our purposes. Almost any soluble form of cellulose dissolved in an appropriate solvent can be employed. Certain cellulose derivatives like hydroxy-ethyl cellulose, which goes into solution in aqueous caustic alkali; solutions of cellulose esters like pyroxylin; viscose solutions (a modified form of cellulose in water solution); and solutions comprising cellulose dissolved with the aid of copper-ammonia reagent or zinc chlorid reagent are all suitable. In each case, on allowing intermingling of the more or less concentrated cellulose solution with water or brine, ordinarily the connate waters in the formations adjacent the well, a form of cellulose or modified cellulose is gradually deposited out. The deposit in each case is of a more or less bulky, fibrous nature and, although quite insoluble, swells with water, increasing the bulk and sealing effect.

Aqueous solutions of cellulose derivatives, and solutions of cellulose materials in organic solvents, are particularly useful for our purposes. There are certain forms of cellulose derivatives which can be put into solution in water, sometimes with the aid of alkali or acid. One such solution comprises viscose. Viscose is a colloidal solution of cellulose, containing a modified form of cellulose, water, carbon disulfid and caustic soda. It is usually made by allowing cotton fiber to swell in caustic soda solution and treating with carbon bisulfid. The product, which may be regarded as a sodium salt of cellulose xanthate, can be dissolved in water or in water

slightly acidified with acetic acid, to form a solution useful for the present purposes. A useful solution for our purpose comprises a mixture of one part viscose with ten parts water, by weight. This solution is readily piped and pumped. Viscose solutions of this description can be diluted with a considerable amount of water or brines without immediate formation of a precipitate, but upon standing the diluted viscose deposits a precipitate; the precipitate presumably comprising a hydrocellulose, together with sulphur. For complete precipitation to occur, a day or so may be necessary. The action is accelerated by warmth, and takes place fairly rapidly in the conditions encountered in deep wells.

In an example of a specific embodiment of the invention utilizing a viscose solution, a well which penetrates both oil and water sands is treated to plug the water sands selectively. Water standing in the well is displaced upward with dry oil. A batch of solution comprising ten parts by weight commercial viscose dissolved in one hundred parts by weight water containing a little acetic acid is injected into the well under high pressure, and pressure is maintained for a day. At the end of this time pressure is released and the well allowed to flow. It is found the water flow is substantially shut off, while oil flow is unaffected.

Caustic soda solutions of certain other cellulose derivatives are likewise useful in the invention. Caustic potash may be substituted for the caustic soda in such mixtures, but caustic soda is cheaper and has certain advantages. While many solutions of cellulose derivatives are gummy and hard to handle, caustic soda solutions frequently have but little viscosity. This is particularly true of solutions of hydroxy-ethyl cellulose; a body which is now made by various methods, including treating moist cellulose with ethylene oxid. This material can be dissolved in 5 to 7 per cent caustic soda solution to give liquids carrying about 0.5 pound per gallon of hydroxy-ethyl cellulose in solution. Such a solution can be used directly in the invention, but somewhat more concentrated solutions are generally more desirable. For example, the solution can contain 10 per cent or more caustic soda by weight and about 0.8 pound hydroxy-ethyl cellulose per gallon of solution. The resulting liquid has a viscosity only slightly greater than that of water and it can be readily pumped, piped and handled. On dilution with water, a flocky and gelatinized clogging body is produced when the concentration of caustic soda drops to about 2 per cent or below. This precipitate swells in place by taking up more water. The presence of salines in the well water does not deleteriously affect the action; flocculation takes place equally effectively with brine.

In practice, any water standing in the well is displaced with dry oil and the treating solution is then injected directly, under high pressure, forcing the waters back into the formations before it. It is not necessary to force back the well waters with fresh water, before injection of the solution, and in fact this is generally to be avoided, as it may cause premature precipitation, or a precipitation in the oil formation where the plastic is not wanted.

In an example of a particular embodiment of the present invention, utilizing alkaline aqueous hydroxy-ethyl cellulose, an oil well penetrating oil bearing and brine bearing strata is freed of

brine and the brine inflow stopped, by pumping in dry oil under pressure. At this time, into the well is forced the described solution of hydroxy-ethyl cellulose dissolved in about 10 per cent caustic soda solution. The cellulose solution enters the wet formations, forcing the brine therein ahead of it without any immediate substantial dilution of the solution in a given pore. The high caustic soda concentration used permits the cellulose solution to be forced back a considerable distance into the water bearing strata prior to the formation of a precipitate. On interrupting the supply of cellulose solution without releasing the pressure, dilution of the liquid occurs by undisplaced brine retained adjacent the pores. When this dilution, which is largely a diffusion phenomenon, reduces the caustic concentration to 2 per cent or less, a voluminous deposit occurs in the pores and swells therein, effectively plugging them. The further back in the formation this plugging occurs, the better, since the pressure differential which the plug must resist, progressively diminishes in going backward. As stated, the precipitated cellulose swells, sealing the pores tightly and resisting dislodgment.

After a pause to allow flocking in the pores, the residual cellulose solution in the well may be pumped out and used elsewhere, being strengthened if it be thought desirable, by solutions of more caustic soda and more hydroxy-ethyl cellulose, either or both.

Other cellulose solutions of this general type are useful, such as alkaline aqueous solutions of so-called oxycelluloses and hydrocelluloses. The oxycelluloses are products formed by the action of certain oxidizing agents on cellulose and the hydrocelluloses are obtained by the action on cellulose of cold, concentrated mineral acids, or by boiling cellulose with acetic acid containing about 2 per cent of sulphuric acid. Both oxycellulose and hydrocellulose prepared in this way can be put into solution by steeping in strong caustic soda solution (approximately 10 normal) and diluting the mixture until the solution is about 2 normal with respect to caustic soda. In this way, as much as 36 per cent of oxycellulose or 33 per cent of hydrocellulose can be held in solution in the diluted caustic solution, at 15° C. Upon further diluting these solutions with water the solubilities decrease sharply. The solubilities also decrease sharply if the alkali concentration is increased or decreased. In other words, the solubility is a maximum in 2N caustic soda solution.

Another modification which is particularly useful in certain relations makes use of certain cellulose derivatives or esters dissolved in an appropriate organic solvent, usually one miscible with water to a greater or less extent. Using this modification, there is injected into the well and the water bearing channels adjacent the bore, a solution of a cellulose ester such as cellulose nitrate or acetate in an organic solvent, usually one of the oxygenated organic type including alcohols, ketones, etc. The solution forces the local water ahead of it in the formation. The solution, on dilution with water, deposits the cellulose ester as a bulky solid body, swelling with the absorption of more water as the solvent disappears. Such a solution in a channel is diluted by diffusion of water into it from adjacent wet rock or earth. When the residual solution is pumped out of the well the plugging of the pores is permanent.

Special ester solutions of a thinness permitting convenient handling may be made of commercial clear varnishes, diluted to appropriate thinness may be employed. Most of the commercial varnishes made with cellulose nitrate (pyroxylin) or cellulose acetate are in dry solvents miscible with water, alcohol or acetone being quite generally used. The commercial varnishes also contain high boiling plasticizers which have no particular effect either way in the present invention and a minor proportion of a "non-solvent" (benzol or gasoline) used to make the varnish less hygroscopic; less sensitive to the action of moisture. These non-solvents in the commercial varnishes are not harmful for the present purposes. They are indeed of some advantage in securing the delayed action desirable in the present invention. For the same reason, in making up special solutions for well plugging it is often advantageous to incorporate a little benzol, say 5-10 per cent, or a miscible gasoline with the compositions.

Before injecting the treating solution, any water or brine standing in the well is advantageously bailed out or is displaced upwards with dry oil poured into the casing. Then, in some embodiments, the waters are forced back into the formation by means of a charge of organic liquid, usually the same solvent as is used in making the treating solution; this being introduced into the well under high pressure. This forces back the water in the channels in the wet formation and is later itself displaced in the same way by the treating solution injected into the well; also under high pressure. This latter penetrates a considerable distance into the wet formation. The previous removal of the water prevents premature precipitation. On ceasing pumping the formation waters gradually mix with and dilute the solution and the cellulosic substance is deposited as a bulky, hydrated, swelling precipitate. Deposition takes place in a zone far back in the formation remote from the well face, where it is most effective in shutting off the water. Completely water-miscible solvents like acetone and ethyl alcohol are satisfactory, while if it be desired to delay deposition as much as possible, less miscible solvents, such as some of the higher alcohols including amyl alcohol can be used. These higher alcohols are often components of commercial varnishes. Some of the high boiling solvents used in varnishes, such as glycol diethyl ether behave in the same way as the higher alcohols; they are miscible with water but much more slowly than ethyl alcohol or acetone. The solvent employed also depends on the type of cellulose derivative or ester selected. The solvent is usually one of the oxygen-containing organic type including alcohols, ketones, etc.

Cellulose acetate dissolved in acetone is useful and cheap. Eight ounces of a certain commercial grade of cellulose acetate can be dissolved in 1 gallon of acetone to form a solution having a viscosity of about 2.6 centipoises at 25° C. (The viscosity of water at this temperature is 0.9 centipoise.) The cellulose acetate in this case is of a "low viscosity" grade, approximately equivalent to that of a 0.5 second nitrocellulose. That is, 0.5 second nitrocellulose dissolved in acetone in similar proportions gives a solution of about the same viscosity.

In general, solutions of relatively low viscosity, of the order of 15 centipoises, more or less, are more convenient to pump and pipe than those of high viscosity.

One convenient source for the cellulose solutions for the present purposes is, as stated, commercial cellulose lacquers or varnishes. These are thinned or diluted with acetone, etc. before use, to reduce the viscosity. Many of these lacquers contain resins in addition to the cellulose acetate or cellulose nitrate; a synthetic resin formed from glycerin and phthalic anhydrid, for example. On dilution with water, these resins precipitate in the same way as the cellulose derivative and while they modify the deposit it is also a good material for plugging pores; it subsequently swells with water in much the same way as cellulose ester alone.

Another good treating solution comprises colloidion (nitrocellulose) dissolved in a mixture of alcohol and ether. This gives the delayed precipitation described. On being left in contact with the formation waters or brines, the solvent is slowly diluted and carried away, leaving the nitrocellulose deposited in the pores. The slow action permits the solution to be forced a considerable distance into the formation before substantial deposition occurs. In using this solution water standing in the well is bailed out and the waters forced back into the formation with a charge of alcohol and ether mixture. Or, because of the slow deposition action, this step can be omitted and the solution forced in directly after the displacement of standing water.

Cellulose acetate dissolved in acetic acid is useful particularly in a modification of the invention adapted for treating difficult cases: high pressure formations and very pervious formations. A solution comprising 5.7 pounds cellulose acetate in 100 pounds 99.5 per cent acetic acid requires dilution with a volume of water equal to the volume of the solution, before any deposition occurs. In ordinary treatment, this solution can be injected into the well immediately after displacing the standing water with oil. No previous forcing back of local water is necessary. In treating high pressure formations or very pervious formations, the waters can be forced back into the formation with acetic acid, and the solution then injected. This allows of the solution being forced a great distance into the formation before deposition occurs. The deposit is formed at remote points, where the pressure gradient is lowest; and opportunity is given for provision of a greater quantity of sealing matter.

In all the cases described there is no tendency for cellulose to be deposited in the oil formation, most of these cellulose ester solutions being immiscible with petroleum oils. Any of the treating solution getting into the oil formation is simply flushed out when the well is allowed to produce.

In an example of a specific embodiment of this modification applied to shutting off water in an oil well penetrating water sands, a batch of treating solution is made up comprising 7.55 pounds commercial cellulose acetate dissolved in 100 pounds acetone. The solution has a viscosity of about 2.6 centipoises at 25° C. It is relatively mobile and can be readily pumped and piped with ordinary oil well equipment. Water standing in the well is displaced upwards with a charge of dry oil. The formation water is now forced back with a charge of acetone introduced under pressure. The solution is then injected under high pressure sufficient to force the solution, with the acetone ahead of it, a considerable distance into the formation. Pressure is maintained for

awhile, and then released. Water flow is found to be substantially stopped.

In another example of a specific embodiment of the invention applied to plugging water sands adjacent an oil well, a batch of treating solution is made up comprising 5 pounds nitrocellulose (tetranitrated cotton) dissolved in a batch of solvent consisting of 50 pounds 95 per cent ethyl alcohol and 50 pounds ether. The solution has a viscosity of about 2.0 centipoises at 25° C. Water standing in the well is displaced upwards with dry oil. The characteristics of this solution are such that precipitation is delayed. Hence it is not necessary to force back the formation water; though this can be done if especially far-reaching sealing is required. In this example, the forcing back step is omitted and the solution is forced in after the displacement step. After awhile pressure is released. It is found that the water flow is practically completely cut off.

In a third example, a well producing water as well as oil from adjacent strata is treated to shut off the water. A batch of 100 pounds commercial clear varnish comprising about 15 pounds of a mixture of cellulose tetranitrate and phenolic esters dissolved in 85 pounds commercial lacquer solvents such as a mixture of ethyl acetate, butyl acetate and ethyl alcohol is cut back with 100 pounds acetone. The well waters are forced back with a charge of acetone injected under pressure and the solution is pumped in under heavy pressure. On release of pressure it is found that the water flow is materially reduced or completely shut off. The treatment can be repeated if necessary.

While the treating solutions can be of high concentration, containing a relatively high proportion of dissolved cellulose, it is generally better to employ the less concentrated solutions. They are easier to pipe, pump and handle and are not so sensitive to precipitation on contact with water. They do not precipitate prematurely. The viscosity of these suitable solutions can range from the minimum possible to the maximum which still allows the solution to be pumped and piped.

When a well is treated with such solutions in the manner described, on dilution of the solution in the pores of the water formation a hydrated cellulosic body is precipitated as a gelatinous deposit which swells on contact with water and plugs the pores and fissures tightly. In all cases, the cellulosic deposit produced in the water formation is highly insoluble in water and hence forms a permanent plug. These cellulose precipitates have a high sealing efficiency; that is to say, the bulk of the precipitate is large for a given weight of cellulose solution.

The solutions described have no corrosive effect on metal parts in the pump and the well and

no special precautions need be taken. Ordinary equipment can be used.

What we claim is:—

1. The method of treating oil wells which penetrate oil and water formations for stopping water inflow to the well without hindering oil flow, which comprises introducing into the well a solution of a cellulose material adapted to deposit out as an insoluble precipitate when diluted with water, maintaining pressure on such material in the well while allowing water in the well to contact with such material to cause deposition, releasing the pressure and allowing the well to flow.

2. The process of claim 1 wherein water standing in the well is displaced therefrom with oil forced into the well under pressure before injection of the solution of cellulose material.

3. The process of claim 1 wherein the solution used is a cellulose material in aqueous solution.

4. The process of claim 1 wherein the solution comprises a cellulose material in an organic solvent.

5. The process of claim 1 wherein the solution comprises a cellulose material dissolved in an organic solution of the oxygen-containing type.

6. The process of claim 1 wherein the solution comprises a cellulose material in alkaline solution.

7. The process of claim 1 wherein the solution used is an aqueous solution of viscose.

8. The process of claim 1 wherein the solution used comprises viscose in water solution in the proportion of about one part viscose and ten parts water by weight.

9. The process of claim 1 wherein the solution comprises hydroxy-ethyl cellulose and caustic alkali.

10. The process of claim 1 wherein the solution comprises hydroxy-ethyl cellulose and caustic soda.

11. The process of claim 1 wherein the solution comprises hydroxy-ethyl cellulose and caustic soda, the caustic soda being in proportion at least 10 per cent by weight of the solution.

12. The process of claim 1 wherein the solution comprises a cellulose material in an organic solvent and the well waters are forced back into formation with a charge of organic solvent before the cellulose solution is injected.

13. The process of claim 1 wherein the solution comprises cellulose acetate in acetone.

14. The process of claim 1 wherein the solution comprises a cellulose derivative dissolved in an organic solvent in proportions such as to secure a viscosity of about 15 centipoises at 25° C., the cellulose precipitating on removal of the solvent as a voluminous hydrated deposit, swelling with water to form a tight seal.

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