

2,219,319

UNITED STATES PATENT OFFICE

2,219,319

TREATMENT OF WELLS

Carroll R. Irons, Midland, Mich., assignor to The
Dow Chemical Company, Midland, Mich., a cor-
poration of Michigan

No Drawing. Application May 18, 1938,
Serial No. 208,603

3 Claims. (Cl. 166—21)

The invention relates to methods of treating wells with a liquid agent. It more particularly concerns an improved method of treating wells wherein a liquid agent is displaced from the well bore and forced into the surrounding formation.

Various kinds of liquid agents are now commonly used in the treatment of wells, such as oil and gas wells in order to facilitate production therefrom and for other purposes. Ordinarily such liquid agents may be sealing agents, useful for sealing the earth formation adjacent the well bore against the infiltration of undesirable fluids; acids useful for creating and enlarging flow channels in acid soluble formations; and paraffin solvents for dissolving and removing accumulations of wax and asphalt in the oil flow channels. All such agents are usually introduced into the well bore and then by the application of fluid pressure are displaced from the bore and forced into the surrounding formation where they are to function. It is the conventional practice to attempt to displace these liquid agents from the well bore by pumping another liquid such as oil into the well on top of the liquid agent until sufficient pressure is developed to cause it to flow from the well bore into the surrounding formation.

I have found that by the foregoing conventional method, it is difficult, if not impossible in some instances, to insure the displacement of the agent from the well bore into the surrounding formation. It often happens that one portion of the formation is more porous than another and the liquid or fluid used as the pressuring medium flows into the porous portion rather than completely displacing or forcing the agent from the well bore into the formation. Such penetration or by-passing of the pressuring medium into the formation often results in the ineffective use of the agent because some of it is thus permitted to remain in the well bore. This by-passing also may cause emulsions to form between the agent and the pressuring fluid, if such liquids are immiscible, because these liquids become intimately mixed in flowing through the small pores and flow channels while entering the formation. Such emulsions tend to plug the pores, seriously restricting the flow of oil to the well after the treatment.

A further disadvantage arises when the liquid to be displaced is a sealing agent of the type which solidifies after standing for a time because that which is not displaced from the well bore forms a solid mass or plug and must be removed by a drilling operation before the well can be

returned to production. Examples of such sealing and earth consolidating agents are the following resin-forming liquids:—unpolymerized styrene and vinylidene chloride, partially condensed phenol-formaldehyde, vinyl esters, and the like. These resin-forming liquids are mobile at ordinary temperatures, but of such a nature that of themselves, or when mixed with a suitable catalyst, or when heated, spontaneously undergo polymerization, condensation, addition, or like chemical action until the whole liquid is transformed into a mechanically strong solid resin. If such a sealing agent is not completely displaced from the well bore, a solid plug forms in the bore which is difficult to remove and necessitates an expensive drilling operation as well as resulting in waste of the sealing agent.

Other difficulties may also arise when employing the conventional method to displace a liquid sealing agent from a well bore depending upon the nature of the surrounding formation. For example, when the formation comprises both relatively permeable and relatively impermeable portions as is usually the case, the liquid agent cannot be uniformly injected into the formation. In the relatively tight portions the penetration of the agent is relatively shallow, while in the more open portions deep penetration is effected. Where such deep penetration occurs the pressuring medium naturally also penetrates into the formation behind the sealing agent causing a separation of the sealing agent in the relatively open portions of the formation from that in the tighter portions. Such separation of one portion of the sealing agent from another prevents the production of a continuous sealing deposit in the formation surrounding the well bore. Consequently, when the injection pressure is released, infiltration can again occur through the unsealed portions between those impregnated by the sealing agent. Thus the discontinuity in the body of a liquid sealing agent resulting from the conventional injection method prevents an effective seal being produced.

It is, therefore, an object of this invention to provide an improved method of displacing a liquid agent from a well bore into the surrounding formation.

Another object is to provide a method of displacing a liquid agent from a well bore, whereby said agent is not forced too deeply into the relatively open portions of the formation while effecting penetration of the relatively tight portions.

Another object is to provide a method of in-

jecting a liquid agent from a well bore into the surrounding formation whereby a continuous sealing deposit is obtained.

Still other objects and advantages will be apparent from the following description of the invention.

Briefly, the method of the invention comprises introducing into the well bore on top of the liquid agent to be displaced from the well bore a quantity of a substantially non-penetrating liquid mixture having about the same or a lower specific gravity than that of the liquid agent. The term "non-penetrating liquid mixture" used herein and in the appended claims means a liquid mixture comprising a dispersion or solution in a liquid of a material which prevents the mixture from penetrating porous formations at relatively high pressures, but which is of sufficient fluidity to be introduced into the well and readily withdrawn therefrom.

Examples of non-penetrating liquid mixtures useful for the purpose at hand are those liquid mixtures having a specific gravity approximately the same as, or lower than, that of the fluid agent to be injected into the formation. One type of such a non-penetrating liquid mixture consists of a solution or a dispersion of an organic jellifying material in water. By "organic jellifying material" is meant an organic material capable of being dispersed or dissolved in water to make a mobile liquid dispersion or solution which exhibits jellifying characteristics after a time. Suitable organic jellifying materials may be prepared from starches, such as those of cassava or rice, by mixing them with water to form a thin paste and boiling the mixture until the starch is hydrolyzed. The cooked starch is dried at about 80° C. and the dried material ground, preferably to a fine powder. The powder so produced may be mixed with water in a concentration of from about 1 to 8 per cent by weight to make a dispersion or solution which possesses suitable non-penetrating characteristics. Another type of non-penetrating liquid mixture having gel-like characteristics may be made by mixing from 3 to 5 per cent of certain soaps, such as aluminum stearate and aluminum palmitate, with liquids, such as kerosene, gasoline and benzene, and preferably crude oil because of its cheapness, and then heating the mixture to from 50° to 80° C.; after cooling to a normal temperature, the mixture is ready for use. Other non-penetrating liquid mixtures may be used for the purpose at hand provided that they are not attacked by the liquid agent to be injected into the formation and do not substantially penetrate into the formation.

After the non-penetrating liquid mixture has been introduced into the well, pressure is then applied upon the mixture to force the liquid agent under it into the formation. The non-penetrating liquid mixture forms a piston-like column in the well bore above the agent to be injected into the formation and as the pressure is applied the non-penetrating liquid mixture descends in the well bore and, since it does not itself enter the formation, it acts as a piston or plunger and displaces the liquid agent below it outwardly into the formation without bringing about the separation of one portion of the agent from another. When the column of non-penetrating liquid mixture reaches the bottom of the well bore the liquid agent is completely displaced from the well bore into the formation. Pressure is maintained on the column, if necessary, to

prevent the agent which has been forced into the formation from returning to the well until such pressure is released. After releasing the pressure the non-penetrating liquid mixture is removed from the well as by bailing or the like.

By the foregoing method thus briefly described it is possible to apply pressure upon a liquid agent introduced into or already present in a well bore so as to force the agent into the formation thus avoiding the aforementioned attendant difficulties. It is also possible to obtain improved results as regards the sealing effect produced when the method is used in conjunction with a liquid sealing agent of the type which spontaneously solidifies after standing for a period of time. For example since the sealing agent is not forced out of or removed from the porous portions of the formation immediately surrounding the well bore by the pressuring fluid flowing into the formation as is generally the case when the conventional method is employed, but instead is just displaced from the well bore without being followed by the pressuring medium, and thoroughly impregnates the porous formation immediately surrounding the well bore, a highly effective continuous seal is produced which extends continuously from the walls of the well bore into the formation. A smaller volume of sealing agent is also required because the area which must be impregnated to produce a satisfactory seal is less, when the seal is continuous and deposited near the well bore than when deposited deeply in the formation in discontinuous portions.

The following is illustrative of a mode of carrying out the invention in shutting off water infiltration in oil wells employing a resin-forming liquid to produce a sealing deposit in the water bearing earth. As the resin-forming liquid there may be employed any one of the following:—

Example 1

Liquid vinylidene chloride is mixed with 0.7 per cent tetraethyl lead, 0.6 per cent of chloro-acetyl chloride and 0.25 per cent of benzoyl peroxide as catalysts to bring about solidification. The resulting mixture remains fluid for about 50 minutes at 100° F. and longer at ordinary temperatures, but gradually solidifies. It may be injected into porous earth or rock within about 50 minutes of the time it is made up and therein becomes a solid resin insoluble in oil or water within about 24 hours.

Example 2

Unpolymerized or liquid styrene is mixed with petroleum oil in amount up to 30 per cent by volume, and about 2 per cent stannic chloride based upon the volume of styrene is added. The function of the petroleum oil is to act as a diluent reducing the speed of polymerization. With no added oil the mixture of styrene and catalyst alone becomes a solid resin in about 2½ hours at 100° F. When from 10 to 20 per cent by volume of oil is present, the mixture becomes solid within 18 hours at 100° F. and with 30 per cent of oil the mixture becomes a semi-hard solid in about 18 hours and becomes quite solid in 30 hours.

Example 3

Mix together 60 parts of styrene (unpolymerized), 30 parts of oil pitch, and 10 parts of petroleum oil, and then add a suitable catalyst in amount such that transformation of the liquid

mixture into a solid resinous body will occur after a predetermined time. Stannic chloride may be used for this purpose, the amount employed being selected so as to bring about the desired polymerization at a convenient rate. The addition of about 2½ per cent by volume of stannic chloride, based upon the volume of styrene, makes a liquid mixture which is quite fluid and remains so for about 90 minutes at ordinary temperatures. The mixture becomes a very strong solid resin insoluble in oil or water within 10 hours.

Example 4

Unpolymerized styrene may be used undiluted and without a catalyst when injected into formations having a temperature of about 150° F. or more, since heat alone brings about polymerization at a rate which depends upon the temperature of the formation. At about 70° F. styrene will remain sufficiently liquid for a relatively long time so as to be pumped through fine pores, but becomes a solid hard resin at a temperature above about 150° F. within 7 days.

Example 5

Unpolymerized styrene mixed with about 2 per cent of stannic chloride by volume remains sufficiently liquid for about 20 minutes to be injected into porous earth or rock and therein becomes a solid resin in about 2½ hours, when the earth temperature is about 100° F., and at ordinary temperature becomes solid within 8 to 12 hours.

In accordance with the invention the resin-forming liquid, for example, is displaced from the well bore into the surrounding formation in the following manner when it is desired to seal a water bearing stratum located above an oil producing stratum. A packer is first run into the well on the tubing and set at a point just below the water bearing stratum. The tubing may then then be disconnected from the packer and withdrawn from the well. A quantity of the resin-forming liquids is introduced into the well bore in amount sufficient to impregnate the surrounding formation. Thereafter a quantity of a substantially non-penetrating liquid mixture is introduced into the well in an amount sufficient to fill the well bore to the top of the section of the formation to be treated. Pressure is applied upon the non-penetrating liquid mixture to force the resin-forming liquid into the surrounding formation.

Any fluid such as air, oil, or water may be used as the pressuring medium for applying the pressure. Pressure is maintained, if necessary, upon the non-penetrating liquid mixture to keep the resin-forming liquid in the formation until set. Setting occurs normally in from about 4 to 48 hours depending upon the kind of resin-forming liquid used. Since the non-penetrating liquid does not enter the formation, the sealing agent is thus caused to impregnate the walls of the well bore forming therewith a continuous sealed mass. After a sufficient time has elapsed for the resin-forming liquid to completely solidify, the non-penetrating liquid mixture may be bailed from

the well and the packer removed, after which the well may be put into production.

Although the method has been described with particular reference to its use in injecting a liquid sealing agent into the formation surrounding a well bore, it is also to be understood that the method may be employed to effect the injection of any other type of liquid agent.

Among the advantages of the invention are that it permits the complete displacement of a liquid agent from a well bore into the surrounding formation, it permits employing a pressuring liquid to effect displacement of a liquid agent from a well bore into the formation without such pressing liquid entering the formation; and it permits a liquid agent to be used in the formation surrounding a well bore with greater efficiency because the liquid does not become separated into discontinuous portions by the pressuring fluid used to effect its injection into the formation.

Other modes of applying the principle of my invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the steps stated by any of the following claims or the equivalent of such stated steps be employed.

I therefore particularly point out and distinctly claim as my invention:

1. In a method of treating the formation surrounding a well bore with a liquid sealing agent, the steps which consist in introducing into the well bore a quantity of a liquid sealing agent, introducing into the well bore on top of the liquid sealing agent a sufficient quantity of a non-penetrating liquid mixture to cover the formation, said mixture having a specific gravity not substantially greater than that of the liquid sealing agent, and applying fluid pressure upon the said mixture, whereby the liquid sealing agent is displaced from the well bore into the surrounding formation.

2. In a method of treating the formation surrounding a well bore with a resin-forming liquid, the steps which consist in introducing into the well bore a quantity of a resin-forming liquid, introducing into the well bore on top of the resin-forming liquid a sufficient quantity of a non-penetrating liquid mixture to cover the formation, said mixture having a specific gravity not substantially greater than that of the resin-forming liquid, and applying fluid pressure upon the non-penetrating liquid mixture, whereby the resin-forming liquid is displaced from the well bore into the surrounding formation.

3. In a method of treating an earth formation surrounding a well bore, the steps which consist in first introducing a charge of a liquid treating agent into the well bore, then introducing into the well bore a quantity of a non-penetrating liquid mixture, and applying fluid pressure above the said liquids in the well bore, whereby the column of non-penetrating liquid is caused to act upon the liquid treating agent to displace the latter from the well bore into the formation.

CARROLL R. IRONS.