

## UNITED STATES PATENT OFFICE

2,349,181

METHOD OF SEALING OR FIXING CASING  
TUBES IN WELLS

William Bruce Lerch, Clyde H. Mathis, and Eugene J. Gatchell, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

No Drawing. Application May 19, 1938,  
Serial No. 208,932

6 Claims. (Cl. 166—22)

This invention relates to a process for sealing off water behind casings in wells and cementing pipe so as to prevent migration of underground water between upper and lower portions of the well hole.

The invention more particularly relates to the use of a liquid material which, after in place, will undergo condensation, association, polymerization or other chemical reactions to form a resin in the space between the casing and the well bore that will prevent the flow of water from water formations into the oil bearing or producing formation.

Moreover, this application is a continuation of our previous application Serial Number 200,766 filed April 7, 1938 wherein the liquid resin material is disclosed for sealing off formations encountered in the drilling of wells but before the well bore has been cased.

The exclusion of water from oil bearing formations is a matter of the gravest importance, not only to the owner of a well in which water may appear but also to the holders of surrounding leases. Water may be frequently encountered in drilling and if it is admitted to the oil sand, permanent injury to the well and adjacent territory inevitably follows. Water entering at a leaky casing seat gradually cuts a channel which admits increasing quantities and if this attains ample volume and reaches a sufficient level in the well, the oil will be drowned or pushed back laterally by reason of the greater specific gravity of water, perhaps permanently ruining the well and flooding a portion of the adjacent territory. Also, water from different formations usually differs in the amount of dissolved materials in said waters, said materials being salts such as sodium chloride, calcium chloride, etc. This difference in amount and quantity of dissolved salts causes a difference in potential between the water producing formations. When the casing is in contact with these waters it completes the circuit for a concentration cell which condition is a well known source of corrosion. The casing thus becomes perforated and allows the waters to enter the well bore through the perforations or corroded spots in the casing.

The exclusion of water by the cementing process, while involving considerable expense and delay, is probably the most satisfactory in regions where wells of large capacity are encountered and a permanent solution of the difficulty is desired. In other fields water is promptly, economically and effectively excluded by means of packers lowered on either casing or tubing. In

the older fields of the United States, the packer method is the one generally used, about thirty types of improved packers now being manufactured to meet the varied requirements. In known regions where wells of large capacity or high pressure are anticipated or where the exclusion of water is difficult, it is customary to cement the water string of casing in the most suitable formation between the oil sand and the last water bearing stratum encountered above it. The objective sought in cementing is to construct a water tight barrier between the exterior of the lower portion of the casing and the wall of the well in order to exclude from the drill hole all water previously encountered.

The primary object of this invention is to introduce a liquid resin forming material, either with or without a filler being added, into the space between the well bore and the casing in such a manner that the resin by condensation, association, polymerization or other chemical reaction, will be formed, thereby plugging the space between the well bore and casing to prevent water from coming into contact with the casing and further to prevent seepage of water into the oil bearing formation from water formations located above the same.

A further object of this invention is to provide a resin forming material which prevents contact between the casing and the source of corrosive water and further acts as an electrical insulating material so that the iron casing cannot serve as a conductor in completion of a circuit in a concentration cell.

A still further object of this invention is to provide a resin forming material which is non-porous and will not permit the seepage of water and also presents a lighter material to pump than a slurry of cement.

A still further object of this invention is to provide a resin forming material which has the advantage of remaining liquid until it is in place and the setting time may be varied or controlled from a few minutes to several days.

Other objects and advantages will appear to those skilled in the art from a careful study of the description to follow.

The resins which are suitable for carrying out the objects of this invention can be either liquid or solid and are usually the products of condensation or polymerization reactions. The products which the invention is concerned with, are those resins that will be solid material at the temperature of formation or surface that is to be made impermeable. The resins should fur-

ther be insoluble and chemically inert in water, brine and acid solutions. Among the resins found most suitable for carrying forward the objects of the present invention are the reaction products of an aldehyde or ketones with thio-phenols, thiocresols, phenols, cresols, urea, thiourea or phthalic anhydride, using a catalyst which may be either alkaline or acid. Muds or fibrous materials may be added to the resin forming material to give it more strength and to make a less expensive material.

The liquid resin materials applicable to this invention may be composed of furfural and carbon disulfide, phenol, urea, thiourea, thio-cresols, thio-phenols or derivatives of these compounds in the presence of a catalyst, either a mineral acid, salts of a weak base and strong acid such as ammonium chloride or alkali, in aqueous solution or other suitable solvents such as acetone, alcohol, glycerol or carbon tetrachloride, if greater weight is desired. Other catalysts may be used particularly when the active components of the solution are in an anhydrous solvent. Catalysts such as sulfur monochloride, thionyl chloride or other compounds having hydrochloric acid in equilibrium or yielding hydrochloric acid on hydrolysis will cause the liquid to resinify. If a catalyst of corrosive nature is employed, satisfactory inhibitors may be added to the liquid without interference to the resin forming action.

Illustrations of the practice of the invention are set forth in the following examples:

A liquid resin forming material applicable to sealing between the well bore and the casing in oil wells may be composed of three parts thiourea, three parts water, three and one-half parts concentrated hydrochloric acid (sp. gr. 1.19), six parts of furfural and 10 parts of a filling material which does not react with the resin. "Aquagel," a product marketed by the Baroid Sales Company and consisting of clay products of which one is bentonite has been found very suitable as a filler material. This liquid mixture forms a very hard black resin which is insoluble in hydrocarbons, water, alcohol, acetone, hydrochloric acid and/or alkali. The setting time is thirty minutes at 150° F. and at room temperature it is too viscous to pump after four hours. The components of the mixture may be varied in wide limits thus controlling the time of set in this manner. It is more desirable to keep the other components approximately in the proportion mentioned and vary the amount of catalyst to control the setting time. When the resin forming material mentioned is mixed with crude oil, brine or liquid hydrocarbons and permitted to stand, the resin settles to the bottom and forms a very hard mass. The material has the advantage of having a greater specific gravity than most oil field brines while the solution forms a very solid, non-porous plugging agent in the presence of crude oil, brine, or liquid hydrocarbons. It is to be understood that the liquid material would function just as well with the filler material omitted but for the sake of economy and to make the use of the material competitive with cement slurry, it may be necessary to add a filler. The filler may be any of the commercial drilling muds or natural clays which do not react with the resin. "Aquagel," above mentioned, is very well suited for this purpose because it does not settle out and a large portion may be added to the resin forming liquid without making the finished product too viscous to pump. Materials, such as

wood fiber or commercial products like desugared sugar cane fibers, make a suitable filling agent. If finely screened sand is applied in a manner that it does not settle out, it makes a very strong sealing material. Carbon black has also been found to be a very desirable and economical filler for the liquid material.

The same mixture as above set forth with the addition of 30% of 95% denatured alcohol increases the setting time to six hours at room temperature, but the resulting resin is not as dense or compact as the original where the alcohol had not been added while the specific gravity is also less.

A liquid resin forming material formed from 3 parts thiourea, 6 parts furfural, 3 parts water, 3 parts 5.4% hydrochloric acid and 10 parts filler forms a very hard mass within thirty minutes at 180° F. while at room temperature the material remains liquid for over two days.

A liquid resin forming material formed from 5 parts furfural, 5 parts mixed cresols, 3 parts of 4% sulfur monochloride in carbon tetrachloride solution, forms a rubber like resin which has desirable characteristics. If desired, any suitable filler may be added to the liquid to make a more economical resin. Equal portions of the filler to the liquid resin forming material is a very suitable mixture and the filler may be suitable proportions of muds, "Aquagel," carbon black, sulfur, or any other suitable filler.

According to the preferred embodiment of this invention, resins quite suitable for plugging between the well bore and casing may be formed from furfural, caustic oil and a catalyst with a filler added to the mix. Caustic oil is a product obtained from the caustic wash of the cracked distillate produced in crude oil refineries, processing particular types of crude oil, such as the caustic oil produced at the Alamo refinery of Phillips Petroleum Company located at Borger, Texas. The exact quantitative analysis of caustic oil is not known but the principal components are thiophenols, thiocresols, phenols, cresols and mixtures of other sulfur compounds. At present this caustic oil material is a worthless product and is discarded. The catalyst used may be hydrochloric acid, sulfur monochloride, ferric chloride, or other materials that will yield hydrochloric acid on hydrolysis or contain hydrochloric acid in equilibrium. Hydrochloric acid is the most suitable catalyst because of its availability and since it is a water solution, fewer mixing difficulties are presented. The filler used may be muds, "Aquagel," carbon black, sulfur or any other suitable material. The setting time is very well controlled by the amount of catalyst used. In mixing these resins a maximum temperature of 120° F. and a minimum temperature of 100° F. is preferred, however these temperatures are given only as examples and are not to be interpreted as limiting the temperature range at which the product may be prepared.

Experimentation has shown that the best ratio of furfural and caustic oil is: furfural, 25 parts; caustic oil, 75 parts, with an equal amount of filler added. This is the ratio which the reaction seems to indicate gives the best results and it is also more economical to use as little furfural as possible since its cost is greater than the caustic oil. However, when a greater specific gravity is desired, the amount of furfural may be increased up to 50% of the solution. The components of the liquid material may be varied within wide limits and still form a resin so that,

any resin from these components is to be considered within the scope of this invention.

When the resin is formed from a 75 to 25 ratio of caustic oil and furfural plus filler, sufficient stirring is required. It is desirable to use efficient agitation for a time, varying between one to four hours. The stirring time may be shortened by the addition of emulsifying agents such as glue, egg albumen, gum arabic, gelatin, or other materials capable of dispersing the acid in the furfural-caustic oil mixture. The addition of gum arabic gives a more elastic product while glue or gelatin gives a very hard dense product.

The setting time of the resin may be varied to fit the particular application, the governing factors being: the depth or extent of the formation, the permeability, porosity and chemical nature of the formation and the available method of application. The setting time is best controlled by the quantity of catalyst present in the mixture.

The resin forming material is applied to the well hole in a manner similar to that used in cementing well casing with cement and the use of the material is to be as a substitute for the presently used cement slurry. The resin forming material in a liquid state must be lowered to the bottom of the well bore within the casing, after which the column of casing is raised a few feet and by mechanical means the material is then forced upward into the annular space between the casing and the surrounding wall and there allowed to solidify. The material may be dumped in the bottom of the hole from a bailer and pressure applied by wooden plugs or any other pressure means available to force the material into the space between the casing and bore wall. The two plug method wherein the material is placed in the casing between two wooden plugs and pressure then applied on the top plug may be employed to get the material into the desired space. The behavior of the material in the liquid state is identical with the behavior of cement slurry and both are adaptable to the same methods for getting the material back of the well casing. The present resin forming material presents advantages over cement slurry in that the time of set can be controlled; when set, the material is non-porous, it is more resilient and will withstand shock better especially when the well is shot and further there is a better cohesion between the material and bore wall and the material and casing. Applicants lay no claim to presenting a new method of getting the resin forming material into the desired space but do present a new method of sealing off the space between the bore wall and the casing.

In conclusion, our invention specifically relates to the use of liquid resin forming materials, with or without a filler added, wherein the chemical reaction is definitely controlled so as to produce a solid resin within a controlled time limit which allows sufficient time to prepare and introduce the liquid resin forming material into a well before the same resinifies or solidifies. Certain chemical mixtures of materials which will react

in this manner have been specifically mentioned but it is to be understood that other compounds or mixtures containing the same physical and chemical properties as those specifically mentioned will react in the same manner as those mentioned and that various changes in the choice and amounts of materials used can be made without departing from the spirit of our invention or the scope of the subjoined claims.

We claim:

1. A method of plugging and sealing the space between the well bore and casing in a well which comprises the step of introducing a liquid resin forming material into the space which consists of a mixture of furfural and thiourea and then allowing the same to solidify.

2. A method of plugging and sealing the space between the well bore and casing in a well which comprises the step of introducing a liquid resin forming material into the space which consists of a mixture of furfural and thiourea to which has been added a catalyst to control the time of set of the liquid resin forming material and said mixture polymerizing to form a solid resin plug in the formation.

3. A method of plugging and sealing the space between the well bore and casing in a well which comprises the step of introducing a liquid resin forming material into the space which consists of a mixture of furfural and thiourea to which has been added an acid catalyst to control the time of set of the liquid resin forming material and said mixture polymerizing to form a solid resin plug in the formation.

4. A method of plugging and sealing the space between the well bore and casing in a well which comprises the step of introducing a liquid resin forming material into the space which consists of a mixture of furfural and thiourea to which has been added a hydrochloric acid catalyst to control the time of set of the liquid resin forming material and said mixture polymerizing to form a solid resin plug in the formation.

5. A method of plugging and sealing the space between the well bore and casing in a well which comprises the step of introducing a liquid resin forming material into the space which consists of a mixture of furfural, thiourea and a filler to which has been added a hydrochloric acid catalyst to control the time of set of the liquid resin forming material, and said mixture polymerizing to form a solid resin plug in the formation.

6. A method of plugging and sealing the space between the well bore and casing in a well which comprises the step of introducing a liquid resin forming material into the space which consists of a mixture of three parts thiourea, three parts water, three and one-half parts concentrated hydrochloric acid and six parts furfural and pressuring the liquid mixture into the space between the well bore and the casing and maintaining the pressure on the liquid mixture until it undergoes a chemical reaction to form a solid resin.

WILLIAM BRUCE LERCH.  
CLYDE H. MATHIS.  
EUGENE J. GATCHELL.