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3,208,525

RECOMPLETION OF WELLS

Filed June 25, 1962

FIG. 2.

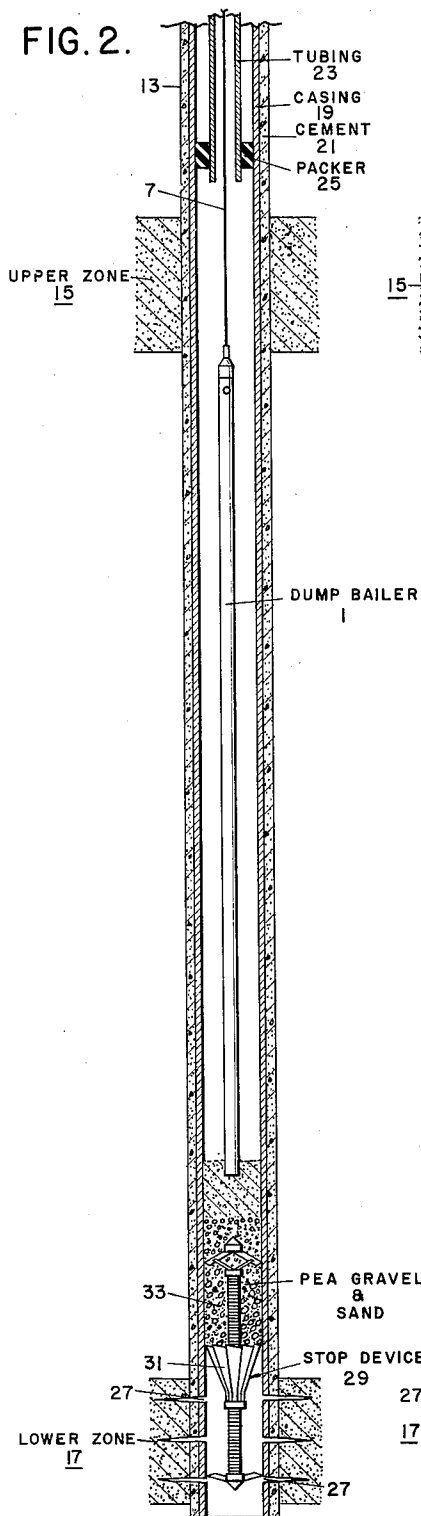


FIG. 3.

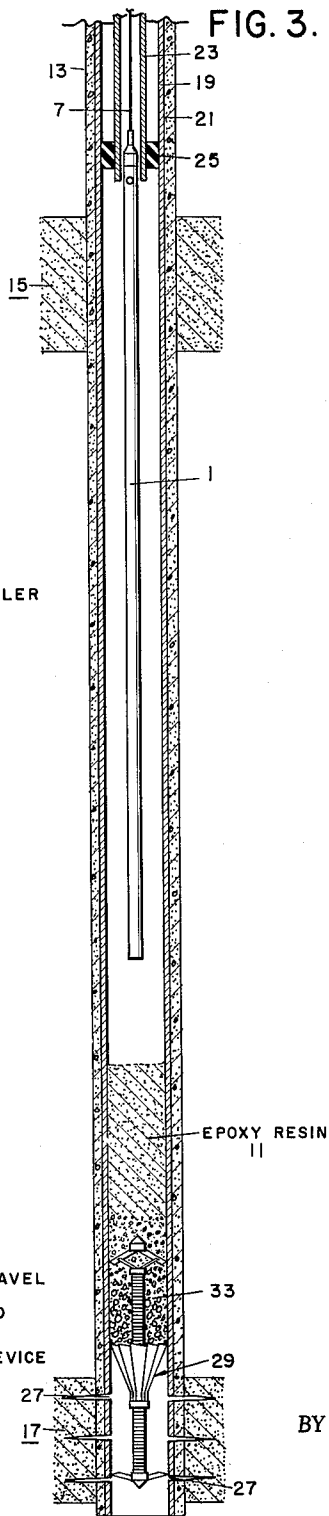
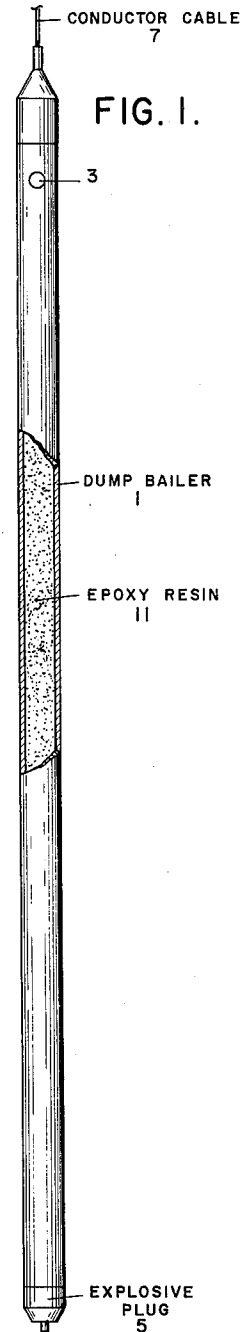


FIG. 1.



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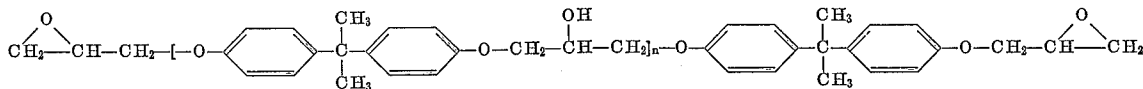
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2 Claims. (Cl. 166—33)

This invention relates generally to recompletions of oil and gas wells, and more particularly to the isolation of fluid productive earth strata which are in fluid communication with the interior of a cased well bore.

After a hydrocarbon productive earth stratum has been produced for a more or less extended period of time, often it is found that the formation pressure has decreased to the point where it is no longer possible to produce fluids from the formation by natural flow. Pumping equipment may be effectively used for a period of time to produce the formation, but eventually the formation will become so depleted that further production is uneconomical. Other factors than pressure maintenance,



such as water intrusion into the well bore, may enter into the decision to no longer produce the formation. On occasion it may be found feasible to produce hydrocarbons from a second earth stratum that intersects the well bore at a higher level than the first earth stratum. It then becomes desirable to isolate the two strata so that the first stratum will not be produced simultaneously with the second stratum. It has been customary in the past to isolate strata by means of strong, heavy bridge plugs, the setting of which requires that the production conduit, or flow tubing string, be pulled from the well.

Recently, there have become available drillable bridge plugs that may be run through tubing strings on a wire line. The use of such apparatus is desirable because the placement thereof is not expensive and does not require recompletion rigs at the earth's surface for pulling tubing and similar operations. Furthermore, the plugs are particularly adapted for use in wells which have been previously set up for permanent-type completion work. These particular bridge plugs all make use of a rather fragile stop device that may be expanded to the interior of the casing string after having been run out of the lower end of the tubing string. When the bridge plug has been set at the desired location in a casing string, a quantity of cement is dumped on top of the stop device and allowed to set. Usually a quantity of pea gravel and sand is dumped ahead of the cement to provide a suitable support plug or base for the fluid cementitious material. Through-tubing bridge plugs are described in some detail in an article entitled "How Through-Tubing Bridge Plugs Work," by Robert W. Scott, at page 141 of the October 1959 issue of the periodical World Oil.

It is manifest that a large differential pressure will be exerted across the set plug inasmuch as the second upper productive formation will have a much higher formation pressure than the first, depleted lower formation. It has been found that such through-tubing bridge plugs often will become loosened as the result of the differential pressure thereacross and will move downwardly so that the two earth strata are brought into fluid communication.

Manifestly, the differential pressure that may be exerted across a bridge plug without the bridge plug becoming loosened will be dependent upon the extent to which the cementitious mixture wets and adheres to the inner surface of the casing and on the area of adhesion.

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Substitution of a fluid material, other than normal Portland cement, that has better wetting and adhering properties manifestly would result in a more desirable bridge plug. In recent years a number of such materials have become available which have been termed thermosetting phenolic condensation resins. Examples of such thermosetting phenolic condensation resins are the condensation products of phenolic bodies with reactive bodies, such as epichlorohydrin (1-chloro-2,3-epoxypropane) and various amines and aldehydes. Thermosetting phenolic condensation resins that have particularly desirable wetting and adhering properties are epoxy resins, which are diglycidyl ethers of polyalcohols or polyphenols such as the product obtained by the reaction between epichlorohydrin and bisphenol A using carefully controlled additions of caustic soda to control the pH by neutralizing the hydrochloric acid formed in the reaction. The pH is maintained below the end point of phenolphthalein, about 8 to 8.5. Bisphenol A is sometimes referred to as 2,2-n-propylidiparaphenol. The epoxy resins formed from bisphenol A have at least two reactive epoxy groups in their molecule and are represented by the formula:

where n is an integer having a value of 1 or a greater number, and are preferred in connection with the present invention. It is usual to use catalytic curing agents known as hardeners or accelerators with the thermosetting resin to catalyze or accelerate the hardening reaction of the resins at low temperatures. At high temperatures, such hardeners are not needed.

Under many circumstances it is necessary and desirable to incorporate a quantity of a filler, such as silica flour, in the thermosetting resin for the purpose of controlling the exotherm developed by the resin-catalyst mixture while it is setting, and for increasing the density of the mixture. For example, manufacturers of epoxy resins have made it a practice to incorporate silica flour mixture in the resins unless purchasers specify otherwise. Unfortunately, the incorporation of silica flour makes the composition susceptible to penetration by water. This penetration appears to be promoted by the water preferentially wetting the silica flour filler and displacing the epoxy upward. The migrating material can become attached to the tubing and casing strings so that they are stuck together, or the tubing or casing could become plugged to prevent production of fluids from the well. In accordance with the teachings of the present invention, a small but effective amount of an organofunctional silane selected from the group consisting of organohalosilanes and aminofunctional organosilanes is incorporated in the epoxy resin-catalyst mixture. It has been discovered that incorporation of these materials unexpectedly prevents penetration by water of the composition.

Objects and features of the invention that are not apparent from the above discussion will become evident upon consideration of the following detailed description thereof when taken in connection with the accompanying drawing, wherein:

FIG. 1 is a vertical cross-sectional view, partially in elevation, of a dump bailer that may be used in connection with the invention; and

FIGS. 2 and 3 are schematic representations of an oil well installation illustrating two of the steps of the method of the invention.

With reference now to FIG. 1, there is illustrated a through-tubing dump bailer suitable for use with the invention. The bailer comprises a housing 1 having a filling window or port 3 at the upper end thereof, and a

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deposition port at the lower end thereof which is illustrated as being sealed by an explosive plug 5. The explosive plug preferably is of the type that is electrically detonated by electrical current from a source at the earth's surface. Preferably, the entire lower end of the housing 1 is opened upon detonation of the explosive plug 5 such that the open lower end of the housing 1 may be considered as the deposition port of the bailer. Electrical current for detonation of the plug may be derived from an electrical source (not shown) at the earth's surface to which the plug is connected by an electrical conductor on cable 7. Within the housing 1 is a thermosetting condensation resin 11 and a catalytic hardener therefor.

As indicated above, the preferred thermosetting condensation resin is an epoxy resin, and preferably an epoxy resin having a viscosity less than 5000 centipoises. When an epoxy resin is used, curing or hardening of the resin may be accelerated in any of the following manners: (1) direct linkage between the epoxide groups by the use of tertiary amines of the general formula R_3N ; (2) linkage of the epoxide groups with aryl or alkyl hydroxyls such as alcohols (ROH), with alcohols and tertiary amines (ROH+ R_3N), or with di- or trihydric phenols $Ar(OH)_2$ or $Ar(OH)_3$; and (3) cross linkage with curing agents such as polyfunctional primary or secondary amines (ROH) (NH_2) or (ROH) $_2$ (NH), with dibasic acids or anhydrides, $R(COOH)_2$ or $Ar(COOH)_2$, with polyfunctional phenols plus curing agent ($Ar(OH)_2$ +amine). In the sense used here, R indicates an alkyl group and Ar is an aryl group.

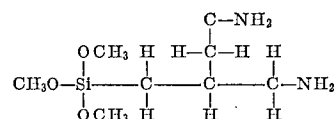
There are many amines, dibasic acids, and acid anhydrides that will serve as catalytic curing agents. Diethylene triamine, diethylamino propylamine, ethylene diamine, triethylene triamine, tridimethylaminomethylphenol, benzyltrimethylamine, metaphenylenediamine, and 4,4'-methylene dianiline, are typical of the amine curing agents for epoxy resins. The acid anhydrides suitable for this purpose are illustrated by oxalic anhydride, phthalic anhydride, pyromellitic dianhydride, and dodecenyl succinic anhydride. A preferred curing agent for use up to 160° F. is 2-ethyl hexoic acid salt of trimethylaminomethylphenol, in a concentration range of 6% to 16% by weight. A preferred curing agent for use in the range of temperatures from 160° F. to 250° F. is 30% by weight of diaminodiphenyl-sulfone along with 1 to 8% of borontrifluoride monoethylamine.

As indicated above, a small but effective amount of an organofunctional silane selected from the group consisting of organohalo silanes and aminofunctional organosilanes is added to the mixture for the purpose of preventing penetration by water of the mixture. Preferably, the amount of silane added is between .05% and 10% by weight of resin.

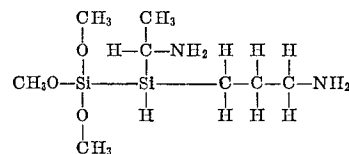
A silane is a direct counterpart of a hydrocarbon having silicon instead of carbon atoms. The generic formula for a silane is $(Si)_nH_{2n+2}$ as compared with C_nH_{2n+2} for a corresponding hydrocarbon. When n is 1, corresponding to methane, a compound is usually called a silane rather than a monosilane. However, when n is 2, the term disilane is applied, when n is 3, the term trisilane is applied; etc. Just as in the hydrocarbons, the hydrogen atoms can be substituted by various groups or other atoms. Thus, a monosilane type of "organosilane" may be designated by the general formulae: $RSiH_3$, R_2SiH_2 , R_3SiH , and R_4Si where the substituting groups designated R may be alkyl, alkoxy, aminoalkyl, or alkeneoxide groups. In general, the substituting groups on the silicon atom will be a mixture of alkoxy and alkeneoxide groups, to promote water solubility, along with alkyl and aminoalkyl groups to promote activity with the resin to give the firm bond between the resin and the casing. To avoid steric hindrance effects, it is desirable to keep the molecular weight of the substituting groups low; therefore, the substituting groups should have less than

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4 carbon atoms therein. Aminofunctional organosilanes having less than 4 silicon atoms, and organohalosilanes are preferred. The preferred organosilane is 2-aminoethyl aminopropyl trimethoxy silane which is represented by the structural formula



Other suitable monosilanes are 2-aminoethyl 2-aminoethyl aminopropyl trimethoxy silane, 2-aminoethyl aminopropyl triethyleneoxide silane, and 2-aminoethyl aminopropyl tripropyleneoxide silane. In all of the above compounds, the aminoalkyl groups can be changed, for example, to 2-aminomethyl aminopropyl, 1-aminoethyl aminopropyl, 1-aminoethyl aminoethyl, and 1-aminopropyl aminoethyl to form satisfactory compounds for use in the present invention. An example of a disilane type of organosilane that may be used with the present invention is 1-trimethoxy 2-aminoethyl aminopropyl disilane, as represented by the structural formula



In the same manner as described in the above example, the ethoxy group, the ethyleneoxide group, or the propyleneoxide group can be substituted for the trimethoxy portion of the molecule. Similarly, the aminomethyl group, the 2-aminoethyl group, or the 2-aminopropyl group could be used, as well as could an aminomethyl, aminoethyl, or aminopropyl group substituted on the second carbon atom of the aminopropyl group.

Also suitable for use are the organohalosilanes illustrated by the generic formulae: $RSiCl_3$, R_2SiCl_2 , and R_3SiCl . In this type of compound, the substituting groups designated R are alkyl groups, and when more than one alkyl radical occurs on the atom they may be the same or different with respect to the number of carbon atoms therein. Examples of suitable organohalosilanes are the following: trichloromethylsilane, dichlorodimethylsilane, trichloroethylsilane, trichloropropylsilane, amyl silicon trichloride, trichloro dodecylsilane, trichloro hexadecylsilane, chlorotrimethyl silane, trichlorophenylsilane, trichlorocyclohexylsilane, trichlorovinylsilane, and dichlorodiphenylsilane. From the above it can be seen that organohalosilanes may be used where the alkyl group has been 1 and 16 carbon atoms therein. In general, compounds having alkyl groups with low molecular weights are preferred because they offer less steric hindrance to the interaction with the resin to generate a firmer bond between the casing and the resin to enhance their utility in preventing water-wetness.

With reference now to FIGS. 2 and 3, there is shown in each figure a typical well installation including a borehole 13 penetrating an upper productive earth formation 15 and a lower productive earth formation 17. A casing string 19 is shown as having been bonded to the sides of the borehole 13 by a cement sheath 21 for the purpose of isolating the various earth formations penetrated by the borehole. This is in accordance with usual practice and will not be further described herein. There is also shown in each of FIGS. 2 and 3 a tubing string 23 having its lower end packed off to the casing by a well packer 25. The casing is shown as having been perforated by a perforating gun or other apparatus to produce a plurality of perforations 27 for the purpose of opening fluid communication between the interior of the casing and the lower productive earth formation 17.

It will be assumed that the lower earth formation 17

has been produced for a more or less extended period of time until it has become depleted. As discussed above, it now becomes desirable to produce the upper productive formation 15 and to isolate the formations 15 and 17 so that they will not be in fluid communication through the bore of casing string 19. To this end a through-tubing stop device 29 is run through the tubing 23 from the earth's surface and is set in the casing between the formations 15 and 17. A particularly desirable stop device includes a metal petal basket 31 which is expandable to the inner surface of the casing string 19. A quantity of pea gravel and sand is dumped on the stop device 29 and is retained above the device by the metal petal basket 31. Preferably, the pea gravel and sand is deposited so that the bottom portion is almost entirely of pea gravel, the top portion is almost entirely of sand, and graduated percentages of pea gravel and sand are therebetween. The combination of the stop device 29 and the pea gravel and sand 33 may be termed a support plug.

At the earth's surface the dump bailer is filled with the desired quantity of resin-hardener-silane mixture. The dump bailer is lowered through the tubing 23 until it is slightly above the upper surface of the pea gravel and sand 33. The explosive plug 5 is detonated so that the resin-hardener-silane mixture will flow from the lower end of the dump bailer. Preferably, the dump bailer is maintained at its initial position for a substantial period of time until as much as possible of the liquid resin-hardener-silane mixture has flowed therefrom. The dump bailer then is very slowly pulled upwardly so as to keep the lower open end thereof (or discharge port) below the surface of the liquid insofar as is possible. This operation is illustrated in FIG. 2. When the entire quantity of mixture has been deposited on top of the support plug, the dump bailer may be retracted up the tubing string as illustrated in FIG. 3.

The resin-hardener-silane mixture should be allowed to set for at least 2 hours after deposition thereof in the well casing. The length of time required for setting of the mixture is determined by the amount of catalyst per unit volume of resin incorporated in the mixture, and by the ambient well temperature of the depth of the plug. In many instances it may be desirable to allow the plug to set undisturbed for as long as 24 or 48 hours to insure complete hardening of the mixture. Thereafter, the casing may be perforated at the level of upper formation 15 so as to open fluid communication between the earth formation 15 and the interior of the casing so that the formation may be produced.

The desirability of including an organofunctional silane when silica flour filler is incorporated in the mixture was demonstrated in the following manner. A plurality of epoxy mixtures were formed, each containing .005 gram of one of a number of water-repelling agents per gram of epoxy resin, were poured into test tubes to a depth of about 1½ inches. Salt water was then poured into each of the test tubes above the resin and the resin was allowed to cure at 170° F. After curing, the depth of water invasion into each of the samples was measured. The

results of these tests are tabulated below. The Dow-Corning Z-6020 listed in the table is 2-aminoethyl aminopropyl trimethoxy silane.

	Depth of penetration (inches)
5 Water-repelling agent:	
Dow-Corning Z-6020	None
Methyltrichlorosilane	None
Epon Agent D	13/16
Sorbitan mono-oleate	1
10 OPE-3 (Rohm & Haas)	13/16
Nonyl phenoxy polyoxyethylene ethanol	13/18
Azelaic acid	1
Dilauryl dimethyl ammonium bromide	13/16
15 Linoleic acid	1 1/8

The invention is not necessarily to be restricted to the sequence of steps, specific structural details, or arrangement of parts herein set forth, as various modifications thereof may be effected without departing from the spirit and scope of this invention.

The objects and features of the invention having been completely described, what we wish to claim is:

1. A method of recompleting a well having a well casing, at a selected earth formation penetrated by the well casing above the level of a previously produced earth formation, comprising: anchoring a support plug in the bore of the casing at a level in the casing below said selected earth formation; forming a mixture of epoxy resin, silica flour filler therefor, a catalytic hardener for said resin, and an organofunctional silane selected from the group consisting of 2-aminoethyl aminopropyl trimethoxy silane, 2-aminoethyl 2-aminopropyl triethoxy silane, 2-aminoethyl aminopropyl triethyleneoxide silane, 2-aminoethyl aminopropyl tripropyleneoxide silane, trichloromethylsilane, dichlorodimethylsilane, trichloroethylsilane, trichloropropylsilane, amyl silicon trichloride, trichloro dodecylsilane, trichloro hexadecylsilane, chlorotrimethyl silane, trichlorophenylsilane, trichlorocyclohexylsilane, trichlorovinylsilane, and dichlorodiphenylsilane in the amount of between .05% and 10% by weight of resin; depositing said mixture on said support plug; and perforating said casing after a time interval of at least two hours from deposition of said mixture.

2. The method of claim 1 wherein the epoxy resin has a viscosity less than 5000 centipoises.

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60 MORRIS LIEBMAN, *Examiner.*