

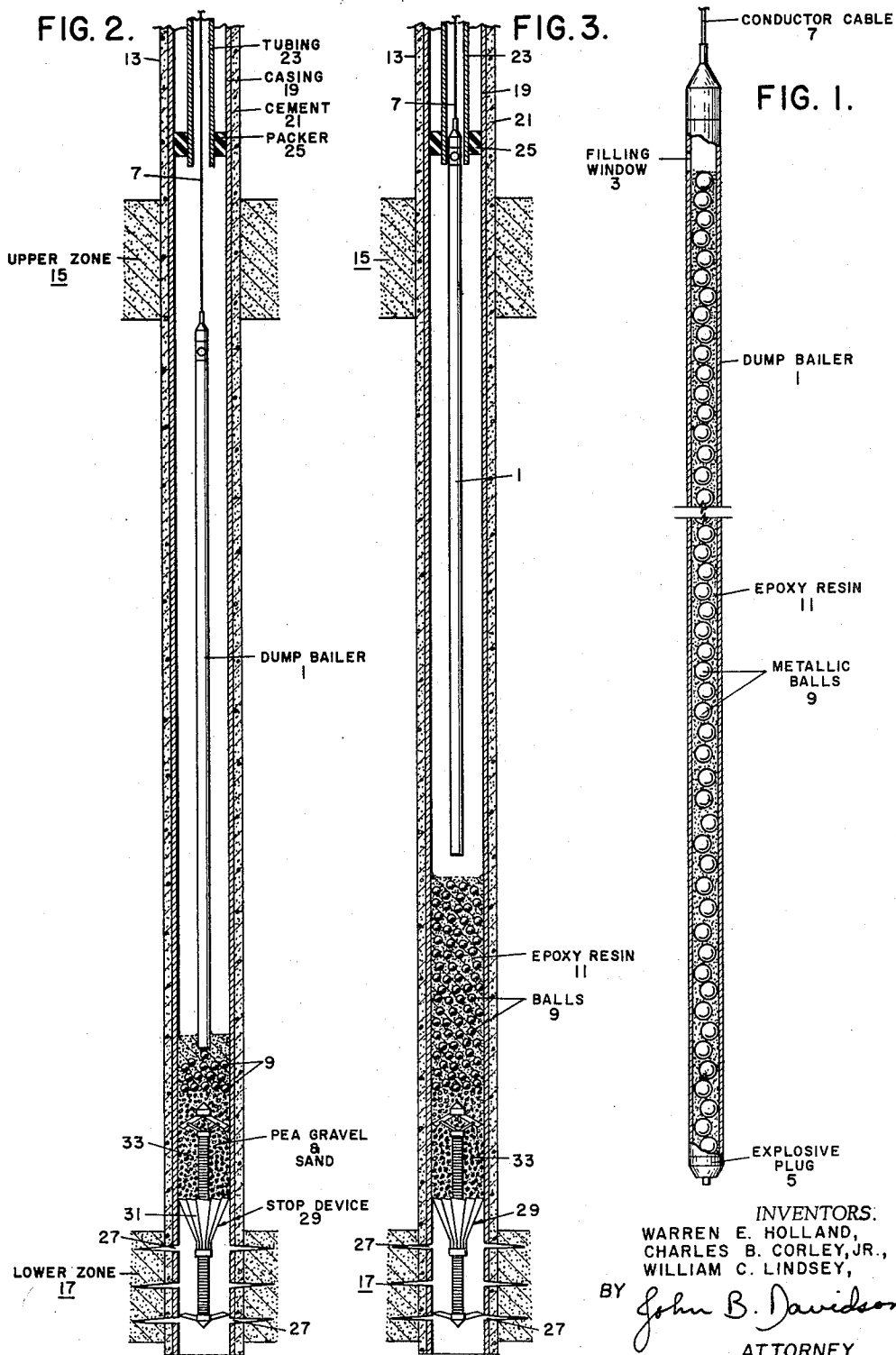
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METHOD OF PLUGGING A WELL BORE WITH A THERMOSETTING RESIN

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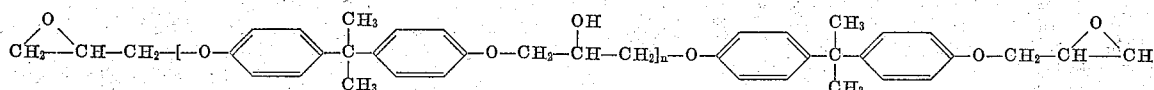
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METHOD OF PLUGGING A WELL BORE WITH A THERMOSETTING RESIN

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This invention relates generally to recompletions of wells, particularly 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 the formation by natural flow. Pumping equipment may be effectively used for a period of time to produce fluids from 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.

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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. Substitution of a fluid material, other than 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, also called 1 chloro-2,3-epoxypropane, and various amines and aldehydes. Other types of thermosetting phenolic condensation resins, types 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 the hardening reaction of the resins at low temperatures.

While the use of such thermosetting condensation resins would appear to give better results in the formation of bridge plugs than would ordinary fluid cement, it has been found that usually such is not the case, particularly when such plugs are set in casings having a diameter greater than about 3 inches. Bridge plugs formed by dumping thermosetting condensation resins and hardeners therefor on a support plug will be found to be characterized by very low strength; such plugs fail at small differential pressures thereacross.

It now has been found, however, that extremely strong bridge plugs may be formed by setting a support plug in a casing in accordance with the prior art, and depositing thereon a quantity of a mixture of a thermosetting condensation resin and a catalytic hardener therefor, along with a plurality of metal balls. Preferably, the balls are spherical and are formed from aluminum, iron, steel, zinc, or copper. The balls should be sufficient in quantity to pack in the resin and hardener from the support plug at least to the top of the resin-hardener mixture. When a dump bailer is used for deposition of the materials, the metal balls should have a diameter at least half the inner diameter of the dump bailer in order to prevent bridging of the balls in the bailer. In depositing the resin and hardener, it has been found that the strength of the bond may be unexpectedly enhanced by keeping the deposition port of the bailer below the surface of the fluid resin-hardener mixture insofar as is possible.

Objects and features of the invention that are not apparent from the above description will become evident upon consideration of the following detailed description thereof

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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 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 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 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 are a plurality of metallic balls 9 and a mixture 11 of a thermosetting condensation resin and a catalytic hardener therefor to accelerate the hardening process.

As indicated above, the preferred thermosetting condensation resin is an epoxy resin, and preferably an epoxy resin having a viscosity less than 5000 cps. When an epoxy resin is used, the 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 ($Ar(OH)_2 + \text{amine}$). 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 curing agents. Diethylene triamine, diethylamino propylamine, ethylene diamine, triethylene triamine, tridimethylaminomethylphenol, benzyl-dimethylamine, 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 diamino-diphenyl-sulfone along with 1 to 8% of borontrifluoride monoethylamine.

While the dump bailer illustrated in FIG. 1 is particularly suitable for use with the invention, it is apparent that other types of dump bailers may be used. For example, under certain circumstances it may be desirable to separate the aluminum balls 9 from the thermosetting resin-hardener mixture 11. In this case a second explosive plug may be incorporated within the bailer and may be separately detonated by electrical energy from the earth's surface so that the resin-hardener mixture may be deposited separately from the balls.

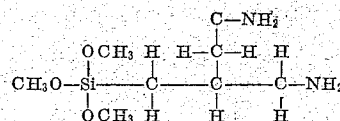
Under many circumstances it is necessary and desirable to incorporate a quantity of a filler such as silica flour in the epoxy resin for the purpose of controlling the exotherm developed by the resin-hardener mixture while it is setting, and for increasing the density of the mixture. Manufacturers of epoxy resins have made it a practice to incor-

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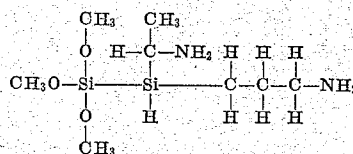
porate silica flour filler in the resins unless purchasers specify otherwise. Unfortunately, the incorporation of silica flour makes the composition susceptible to penetration by water. This penetration appears to be promoted by the water preferentially wetting the silica flour filler and displacing the epoxy upward. It is evident that this condition is highly undesirable. It has been found that the addition of a small but effective amount of an amino-functional organosilane or an organohalosilane will prevent water from penetrating the epoxy resin-silica flour mixture. Preferably, the amount of organofunctional silane 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 alkyleneoxide 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 4 carbon atoms therein.

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



Other suitable monosilanes are 2-aminoethyl 2-amino-propyl triethoxy silane, 2-aminoethyl aminopropyl triethyle-oxide silane, and 2-aminoethyl aminopropyl tripropylene-oxide 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 an aminofunctional disilane type of organosilane that also may be used 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 groups 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, chlorotrimethylsilane, trichlorophenylsilane, trichlorocyclohexylsilane, trichlorovinylsilane and dichlorodiphenylsilane. From the above it can be seen that organohalosilanes may be used where the alkyl group has between 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 further 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 33 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 mixture and metal balls. Preferably, the metal balls are sufficient in quantity so that when the resin-hardener mixture and the balls are deposited on top of the pea gravel and sand 33, the metal balls will pack above the support plug and will extend from the pea gravel and sand to the top of the resin-hardener 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 epoxy resin 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 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 possible, thus permitting all of the metal balls to fall out, along with such of the resin-hardener mixture as remains in the bailer. This operation is illustrated in FIG. 2. When the entire quantity of resin-hardener mixture and the balls have been

deposited on top of the support plug, the dump bailer may be retracted up the tubing as illustrated in FIG. 3.

The resin-hardener 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 at 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 cementitious mixture. Thereafter, production may be initiated from formation 15 by perforating the casing 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.

It has been found that bridge plugs formed in the manner described above are more than three times as strong as a cement plug of equivalent surface area in adherence with the interior of the casing. The reason that the plug formed in the manner described above is strong relative to a plug formed without the use of metal balls is believed to be as follows. The reaction between the thermosetting epoxy resin and the hardener is exothermic so that a great deal of heat must be dissipated if the temperature of the mixture is not to rise excessively. When the resin-hardener mixture sets rapidly at a temperature much higher than its environment, it will shrink on cooling to such a degree that it will at least partially separate from the casing, particularly when the casing has a diameter greater than about 3 inches. However, when metal balls are included in the mixture, a large portion of the generated heat will be absorbed by the balls so that the mixture will not rise to an extremely high temperature. This does not completely explain the magnitude of success obtained by the method, but it is at least a partial explanation thereof.

The desirability of depositing the resin-hardener mixture by keeping the deposition port below the upper surface of the mixture insofar as possible has been experimentally established. It is believed that, as the resin fills the casing displacing water upwardly, the resin preferentially wets the casing and wipes away any water previously wetting the pipe. It has been established that when the resin-hardener mixture is simply dumped through water to the support plug, a water film is trapped between the water and the interior of the casing, thus decreasing the area of contact between the resin-hardener mixture and the casing. The desirability of depositing the resin-hardener mixture in the manner described was established by the following experiment. Two sets of test pipe nipples were filled with saturated salt water. In the first set the epoxy resin-hardener mixture was deposited in the bottoms of the pipes with a burette, the opening of which remained below the surface of the liquid mass. In the second set of pipe nipples the liquid mixture was dropped through the salt water and allowed to settle to the bottom. Enough resin-hardener mixture was placed in each of the pipes to form a plug 1½ inches long. The samples were tested after curing for 24 hours at 150° F. by determining the hydraulic pressure required to extrude the plugs from the nipples. The samples which were dropped through the water failed at an average pressure of 350 p.s.i., while those deposited in the manner described above failed at an average pressure of 2470 p.s.i.

The desirability of including an organo-functional silane when silica flour filler is incorporated in the mixture was demonstrated in the following manner. Epoxy mixtures containing .005 gram each of a multiplicity 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.

Water-repelling agent:	Depth of Penetration (inches)	
Dow-Corning Z-6020 -----	None	5
Methyltrichlorosilane -----	None	
Epon agent D -----	1 $\frac{3}{16}$	
Sorbitan mono-oleate -----	1	
OPE-3 (Rohm & Haas) -----	1 $\frac{1}{16}$	
Nonyl phenoxy polyoxyethylene ethanol ----	1 $\frac{1}{8}$	10
Azelaic acid -----	1	
Dilauryl dimethyl ammonium bromide ----	1 $\frac{1}{16}$	
Linoleic acid -----	1 $\frac{1}{8}$	
Humble "Corexit" -----	1 $\frac{1}{8}$	15

To study the amount of the exotherm and to study its effect on the bonding of the resin to the pipe, a group of experiments was done in 5 $\frac{1}{2}$ inch casing to more nearly simulate actual well conditions. In these experiments 1-foot plugs of epoxy resin were poured into the 5 $\frac{1}{2}$ inch casing and held in a bath at 150° F. In half these plugs, one inch aluminum spheres were used to fill the resin, and in the other half there were no aluminum spheres. During the curing period of 24 hours it was found, by using thermocouples in the resin mass, that when no aluminum spheres were included the exothermic nature of the polymerization caused the temperature to rise to above 212° F. In contrast, those plugs that contained the aluminum spheres heated only to 170° F. After the heat from the reaction was dissipated into the bath and the plugs cooled to 150° F., it was found that one that had heated to above 212° F. had contracted away from the pipe and allowed water to flow freely past the plug. The plugs that contained the aluminum spheres sustained a pressure differential of 550-1000 p.s.i. before failure. This pressure at failure is contrasted with 180-275 p.s.i. for portland cement, the material normally used in plug-back operations in wells.

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 plugging the bore of a well pipe having a support plug secured therein at a predetermined level, comprising:

depositing on said support plug a quantity of a liquid mixture of a thermosetting phenolic condensation resin and a catalytic hardener therefor, and a plurality of metallic balls sufficient in number to be interspersed through said mixture to the surface thereof; and

delaying production of the well until said thermosetting phenolic condensation resin has hardened.

2. A method of plugging the bore of a well pipe having a support plug secured therein at a predetermined level, comprising:

forming a liquid mixture of a thermosetting phenolic condensation resin and a catalytic hardener therefor; depositing said liquid mixture on said support plug along with a plurality of metal balls sufficient in number to be interspersed throughout said liquid mixture to the surface thereof; and

delaying production of the well until said thermosetting condensation resin has hardened.

3. A method of plugging the bore of a well pipe having a support plug secured at a predetermined level therein using an elongated dump bailer having a diameter less than the well pipe and having an ejection port for liquid contained therein, comprising:

with said dump bailer, depositing on said support plug a mixture of a normally liquid epoxy resin, a catalytic hardening agent therefor, and a plurality of metal balls having an outside diameter not less than half the inner diameter of the dump bailer and sufficient in number to be interspersed through the epoxy resin and hardener mixture to the surface thereof; and delaying production of the well until said liquid epoxy resin has hardened.

4. A method of plugging the bore of a well pipe having a support plug secured at a predetermined level therein using an elongated dump bailer having a diameter less than the well pipe and having an ejection port for liquid contained therein, comprising:

with said dump bailer, depositing on said support plug a mixture of a thermosetting phenolic resin and a catalytic hardening agent therefor while insofar as possible keeping the ejection port of the dump bailer below the upper surface of the deposited mixture; interspersing a plurality of metal balls in the deposited mixture sufficient in number to be interspersed through the mixture to the surface thereof; and delaying production of the well until the thermosetting phenolic resin has hardened.

5. The method of claim 4 wherein the metal balls are carried within the dump bailer and have an outside diameter not less than half the inner diameter of the dump bailer.

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