

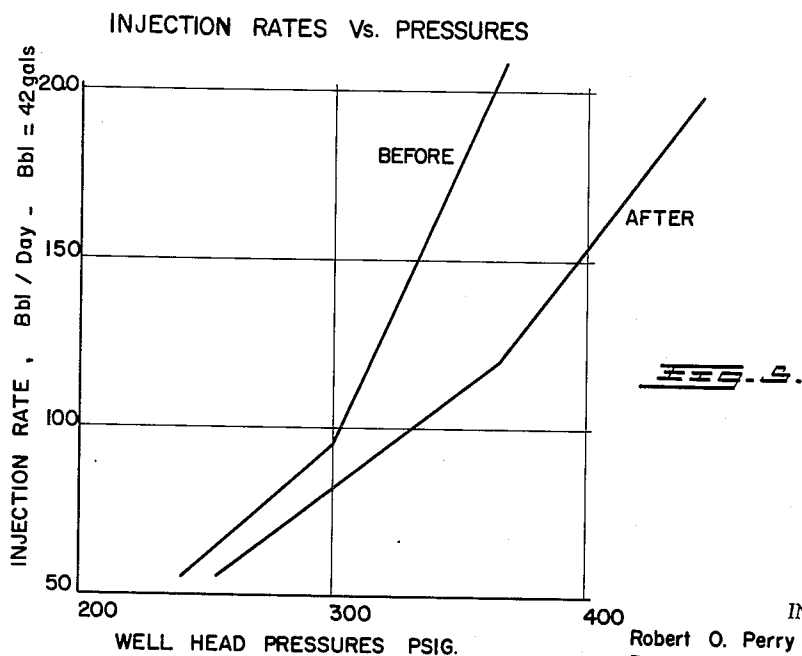
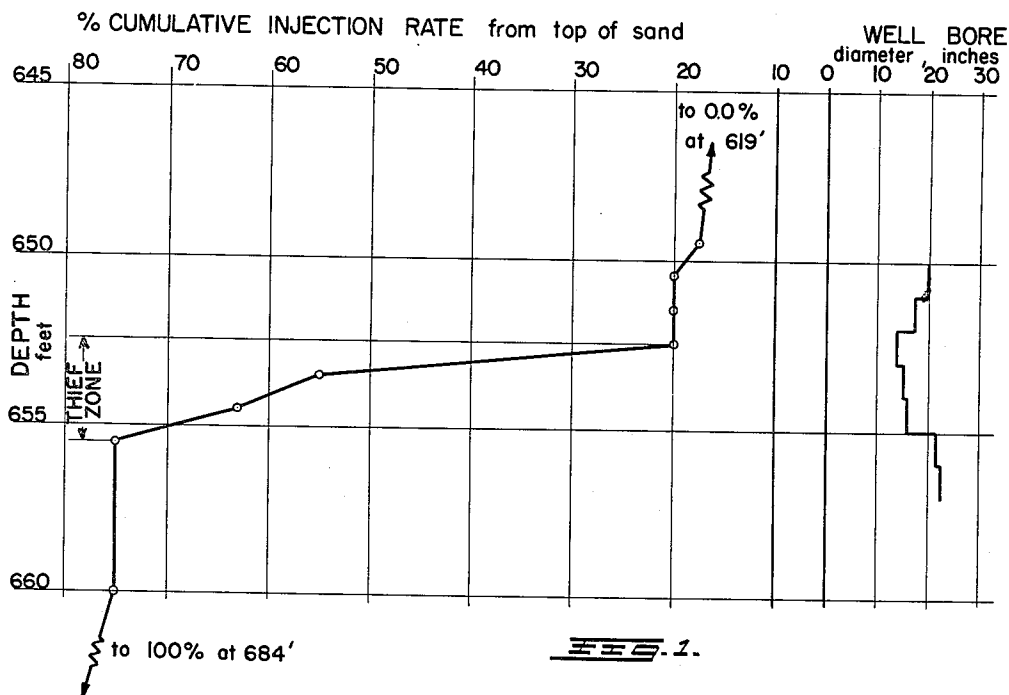
July 17, 1962

R. O. PERRY ETAL
METHOD FOR SELECTIVELY PLUGGING A SUBTERRANEAN
LOCATION IN A WELL WITH LIQUID ORGANIC
RESIN-FORMING MATERIAL

3,044,548

Filed Feb. 27, 1957

3 Sheets-Sheet 1



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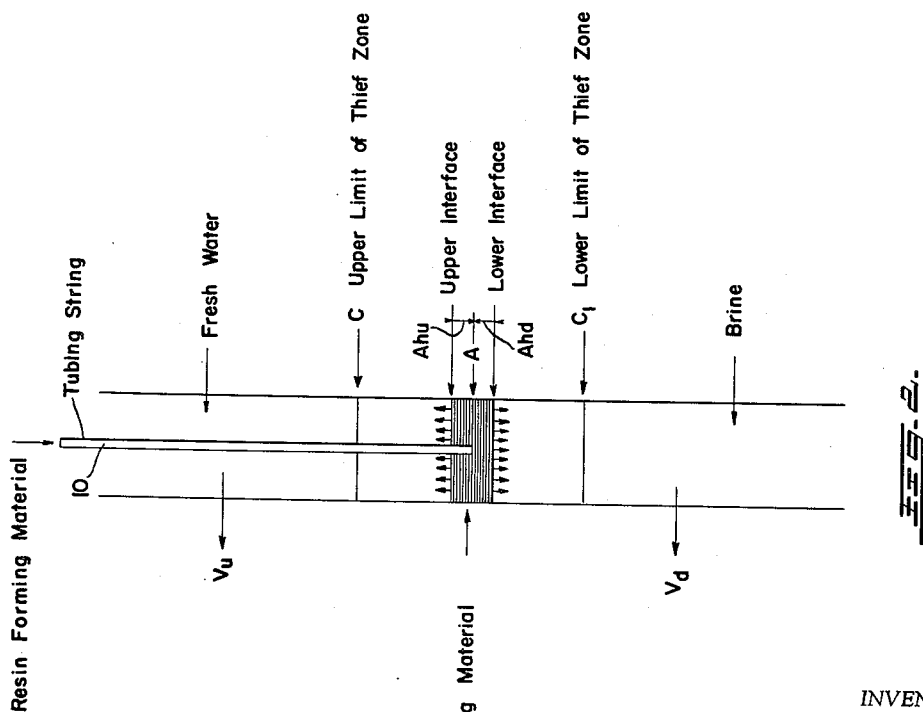
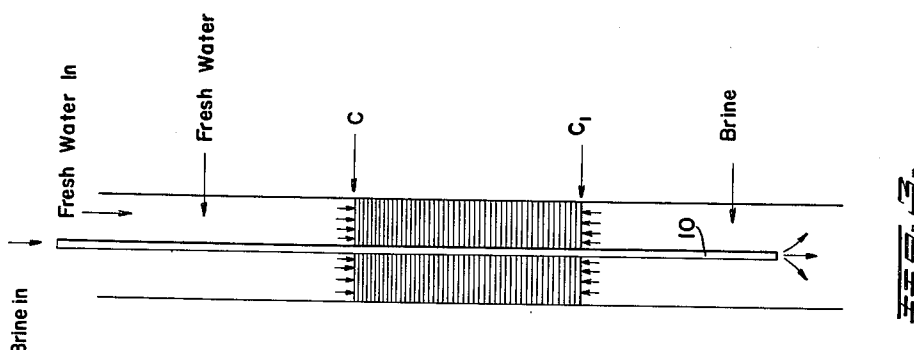
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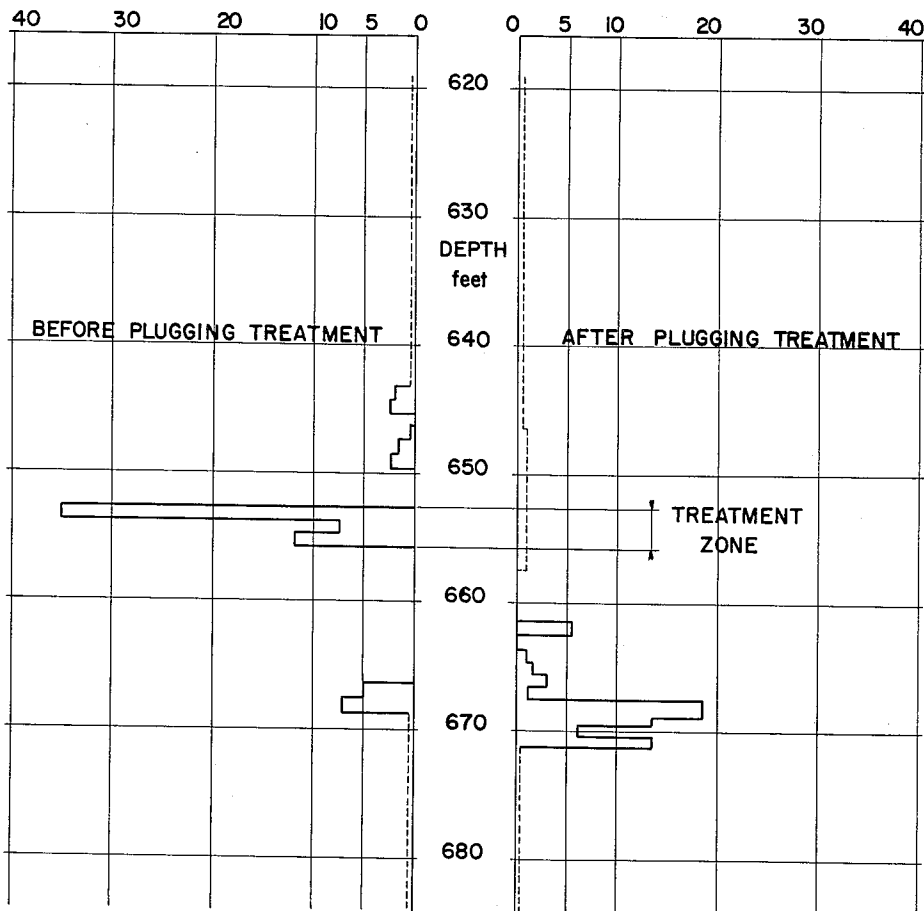
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3 Sheets-Sheet 3

WATER INJECTION PROFILES

% INJECTION PER FOOT OF SAND



LEGEND

- % Injection calculated from injection into each foot increment
- Average % Injection calculated from injection into a sectional sand thickness of several feet increment

Fig. 4.

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1

3,044,548

METHOD FOR SELECTIVELY PLUGGING A SUBTERRANEAN LOCATION IN A WELL WITH LIQUID ORGANIC RESIN-FORMING MATERIAL**Robert O. Perry, Don R. Holbert, and George A. Zeito,**
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15 Claims. (Cl. 166—33)

This invention relates to a method for selectively plugging a location in a well, for instance a permeable subterranean area adjacent a well bore traversing an oil bearing formation, a casing hole or any other relatively permeable area opposite a well bore. More specifically, this invention is concerned with a method of partially or completely plugging a permeable subterranean well area by depositing an organic resin-forming material in the permeable location to facilitate plugging of the desired area without unduly restricting the permeability of overlying and underlying locations.

Our method can be employed in plugging a permeable well location for any reason but advantageously it can be intimately associated with secondary recovery operations for obtaining oil from partially depleted formations, which operations are increasingly important as new oil fields become more difficult and costly to find. Generally, such operations contemplate repressuring an oil-bearing stratum by injecting a pressuring medium into one or more intake wells disposed near one or more producing wells. Water, gas, hydrocarbon or another chemical, for example, is pumped into an intake well under pressure and flows through the oil-bearing stratum to drive the oil toward the producing well from which it can be recovered. One difficulty involved in this method of secondary recovery is that the oil-bearing stratum, e.g. sandstone or limestone, has areas of varying permeability and hence the pressuring medium tends to flow primarily through zones of high permeability and to by-pass the oil-bearing sands or zones of low permeability. Consequently, the oil content of the higher permeability areas is reduced while ineffective recovery is obtained from the low permeability areas. Thus recovery operations incorporating this technique may not be economically successful since large amounts of water must be pumped through the high permeability areas to drive any of the oil from the low permeability areas. The cost of pumping the pressuring or driving medium can even exceed the value of the oil obtained, and in any event the recovery operation is highly inefficient.

To avoid this undesirable result, it has been proposed to isolate or pack-off the high permeability well area and then pump any one of a variety of cementing materials to the area for plugging purposes. This procedure can be practiced rather successfully in wells of substantial diameter, for instance 6 to 8 inches. However, the method is impractical in many input wells where the accessible diameter is in the range of only about 1½ to 4 inches because of drilling, completing and equipment costs. Actually, there are a great many input wells having an accessible diameter of less than about 3 inches. When selected areas of wells having an accessible diameter of less than about 3 to 4 inches are to be plugged, procedures heretofore proposed become impractical due to limitations on the minimum size of packers, handling equipment, etc., which are necessary to the isolation of the well area and the injection and location of the cementing or plugging material. Also, methods depending upon

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the use of packers are not successful where the bore hole area to be isolated is irregular, for instance due to shooting, as an effective seal cannot be made.

The present invention relates to a method for plugging selected portions of a well area which is particularly useful in wells with small diameters, that is where the accessible well, casing or tubing is less than about 3 or 4 inches in diameter, although the method can be employed in bores of any given size. In this method there is no requirement that the bore wall be smooth as no packers need be employed. In the operation the area to be plugged must first be located as to its vertical position in the well bore. This area is spaced away from the bottom of the bore and generally will be between two adjacent areas of lesser permeability although this is not an absolute necessity. Salt (NaCl) water or brine is then provided in the well bore in an amount sufficient to reach the approximate location of the area to be plugged. The level of the salt water can be at or slightly below or above the plugging area but it should not be vertically displaced a distance from the area such that substantial plugging occurs in locations where it is not desired. The salt water can be added as such to the well or fresh water can be injected which after remaining a sufficient period in the bore will become salty due to the presence of salt in the earth's strata. After the proper level of salt water is established an organic resin-forming material is positioned on this medium. Preferably, the salt water layer is below a fresh water layer with these materials forming an interface in the approximate location of the permeable area, and in this case the resin-forming material is positioned on the salt water layer and thus in the interface between these layers. The resin-forming material is then displaced into the adjacent well area or stratum as by natural flow or by a separately applied gaseous or liquid pressure and allowed to remain in the area to set up or harden to provide a partial or complete plug resistant to the flow of fluids, particularly liquids. The method of the present invention is capable of rather wide variations as will be noted in the description which follows.

In locating the permeable area to be plugged any desirable procedure can be employed. Conventional methods concern the use of liquid-to-liquid interfaces between two dissimilar liquids such as water and oil, fresh and salt water, and radioactive and non-radioactive liquids, e.g. see U.S. Patents Nos. 2,376,878 and 2,413,435, and Pfister, R. J., Trans. A.I.M.E., vol. 174, page 269, 1948, to determine the injectivity profile or liquid injection characteristics of the well or sand face. When the interface is positioned adjacent the permeable area the level of the interface can be detected by lowering a suitable device through the interface which provides an indication at the earth's surface as it passes through the interface. Such devices are well-known in the art. Since in our method a layer or column of salt water is to be disposed in the lower part of the well bore, we find it highly advantageous to locate the area to be plugged by one or a combination of the fresh water-brine interface methods.

This interface can be formed and located in the manner desired and commonly either one or both of the so-called moving or stationary interface methods is employed. As an example in the moving interface method the well bore is filled with salt water to above the permeable area to be plugged which can be done since the general location of the area is usually known and then fresh water is fed to the well above the salt water. As the fresh water is injected, the rate at which the salt water-fresh water interface drops is correlated with the amount of fresh water flowing to the well to determine the relative permeability

or tendency to receive fluids at the various vertical positions in the bore.

The stationary interface method can be effected by placing a tubing in the well which extends to below the desired location of the interface. Salt water is then injected down the tubing and fresh water is added around the tubing, for instance at the well head, which provides the interface at a level dependent upon the relative flows of the separate aqueous streams and the permeabilities of the bore well wall areas. By varying the rates of entry of fresh water and salt water, the stationary interface is then formed at a plurality of vertical levels above the end of the tubing whose position can be changed as required to permit the forming of the stationary interface at positions more or less vertically across the entire well face. By detecting the various positions of the stationary interface and correlating them with the flow rates of the separate aqueous streams necessary to provide the interface at a given level, the relative permeability at the various well depths can be determined. As several methods for forming and positioning interfaces in determining the location of permeable areas in a well are known, further discussion is not necessary, but in general these procedures are designated as injection profiling methods.

Upon locating the area to be plugged a layer or column of salt water is provided in the well bore to the vicinity of this area. We can employ the layer of brine previously used in locating the permeable area by the interface method. Also, the water charged could be fresh if allowed to sit in the well bore until enough salt is dissolved to form the desired brine.

The liquid organic resin-forming material deposited on the salt water layer is of the type which has sufficient working time to permit its displacement into the permeable area to be plugged before hardening into the solid or semi-solid state. Unless the material is light enough to remain upon the surface of the salt water which has a specific gravity greater than 1, generally at least about 1.2, it must be quickly displaced into the permeable area before it can disperse into the salt water phase or an overlying fresh water layer, if any be present. To reduce the chances of this happening, resin-forming materials having specific gravities of up to about 1.18, preferably up to about 1.13, can be used. Also, as it is most advantageous to locate the resin-forming material between the salt water layer and an overlying fresh water column, the resin-forming material preferably has a specific gravity of at least about 1.07, more desirably at least about 1.11. The specific gravity of the resin-forming material can be adjusted by the addition of weighting agents.

In order to provide time to place the resin-forming material in the bore hole and displace it into the adjacent permeable area, the material should have a satisfactory working life. In general, the working life of the material at the temperature and pressures encountered in the bore hole is such that it has a viscosity of up to about 10 or 15 centipoises, advantageously about 1 to 5 centipoises, at these conditions for at least about 15 minutes, and preferably for at least about 30 minutes. When referring to "working life" we mean the time which elapses after all ingredients, for instance monomer, catalyst, promoter, etc., of the material have been added which are essential to the formation of the solid or semi-solid plugging resin or plastic under the conditions of temperature and pressure found in the area of the well bore to be plugged. In general, the resins are formed by the interaction of one or more monomeric or resinous materials through polymerization or condensation reactions which form products inert to the chemical and physical action of materials generally present in or added to oil wells. Thus the solid resinous materials in a given instance should not be removed by contact with fluids subsequently employed to treat the well such as water, gases, acids, caustics, and crude oils, or by the release of reservoir pressure. Under given circumstances it may, however, be desired to plug

a well with a material which can be removed partially or completely by contact with a particular treating agent where a permanent plug is not wanted. After the working life of the resin-forming material is passed it goes to a solid or semi-solid state which can provide the effective partial or complete plugging of the permeable area and usually this is within about 1 to 24 hours or more, preferably within about 6 hours, after all of the ingredients of the resin-forming material have been combined.

As stated the resin-forming material can be placed on the salt water layer and preferably it is located between the salt water and an overlying fresh water column. In this procedure a tubing is usually strung to the vicinity of the salt water-fresh water interface and the resin-forming material injected therethrough. When the resin forming material has a specific gravity between about 1.07 and 1.18, the point of deposition in the bore may vary somewhat as the material will tend to become positioned between the water layers. If the resin-forming material is of other specific gravity it is best to deposit it on the salt water layer or at the interface between the fresh and salt water, if there be one, and then displace it quickly into the permeable area before it is unduly dispersed into an adjacent aqueous phase. If the resin-forming material enters the well fluid too far from the interface, there will be a tendency for it to be deposited on the casing or sand face at locations other than that desired, that is other than in the approximate area of the upper level of the salt water. Preferably, the resin-forming material is placed at or slightly above the interface between fresh and salt water, if one be present.

When depositing the resin-forming material in the well one or both of the salt water and fresh water flows can be stopped. Frequently, when the well diameter is limiting and the resin-forming material is to be placed between fresh and salt water, the flow of salt water through its tubing to the lower layer is stopped, the tubing is raised to a point at or just above or below the upper layer of the salt water, and the resin-forming material is carried down this tubing and followed by a salt or fresh water flush if desired.

After the resin-forming material is located on the salt water layer opposite the permeable area to be plugged, the material is then moved into the area before its viscosity is above about 10 or 15 centipoises, preferably the viscosity is from about 1 to 5 centipoises. This movement can be accomplished through its natural flow characteristics since it is opposite the permeable area which may have relatively low pressure drop characteristics or resistance to flow. It is usually better, however, to pressure the resin-forming material into the adjacent area. As an example, the salt water layer can be located at or near the lower boundary of the permeable area and then raised by addition of an aqueous medium, e.g. salt water, through a tubing extending into the lower layer. In this operation the resin-forming material would traverse the permeable area and be displaced into it as the level of the salt water rises. Although if the resin-forming material be located between salt water and an overlying fresh water column, an aqueous medium could be added to the fresh water layer or to both of the aqueous layers to effect a squeezing of the resin-forming material into the permeable area. As stated when the resin-forming material is placed in the permeable area, it is preferred that its viscosity not be above about 5 centipoises, and advantageously the initial viscosity should be close to that of water in order that the material can be forced easily into the area to be plugged. Simple surface tests can be conducted to establish under bore hole conditions the relationship between the viscosity of the resin-forming material and the time elapsed after its components are mixed. After the resin-forming material is in the permeable area it is allowed to set to the solid or semi-solid plugging state. This is easily accomplished, for instance by shutting off all flows to the well for the required time,

Usually the resin-forming material is charged to the bore at a rate faster than it will pass into the adjacent formation. Thus, a layer of the material will be formed. It is frequently advantageous to know that the resin-forming material is at least approximately opposite the permeable area which is to be plugged before this material is displaced into the adjacent well area. The procedure for locating the position of the resin-forming material in the well bore can be varied. For instance, the characteristics of the material can be such that it is detectable by an electrical conductivity profiling unit when the material is placed on the salt water layer or between the salt water-fresh water columns. Thus, if the resin-forming material be essentially electrically non-conductive the conductivity profiling instrument will indicate distinct degrees of current flow when it enters the salt or fresh water layers on either side of the resin-forming material.

For instance, in a typical field operation the brine layer will have a conductance of about 460 milliamps at 6 volts while the fresh water will indicate a conductance of about 120 milliamps at this voltage. Thus, in order for the conductivity circuit to distinguish between the fresh water, brine and resin-forming material, the latter must be essentially non-conductive at the applied voltage. When the conductivity circuit is essentially null then the instrument is in the layer of resin-forming material and by checking the depth of the detecting instrument the location of this layer is determined. Should the layer not be opposite the area desired to be plugged, fresh water can be added around the well tubing to depress the level of the layer or salt water can be added through the tubing to the lower brine layer in the well to raise its level as desired. Thus the layer of resin-forming material can be located opposite the area to be plugged either by merely placing the material in this area or by following the placing with regulation of the position of the layer through salt or fresh water addition if such regulation be necessary. Also it may be desirable to keep determining the location of the resin-forming material as it is being moved into the formation in order to be sure that it is at the proper level; if it is not at the desired location, adjustments in the fresh or salt water flows may be in order. The location of the resin-forming material becomes more unpredictable during its discharge from the well bore, the greater its viscosity differs from that of water since usually the permeability or injection characteristics of the bore have been determined while using aqueous media.

The liquid organic resin-forming materials of our invention can be varied widely as to chemical composition and generally these materials set or harden into rigid or semi-rigid structures. Of course, the resin-forming material must have the noted viscosity characteristics during a substantial working life so that it can be moved into the permeable well area and preferably the specific gravity is from about 1.07 to 1.18 as previously stated. The resin-forming material can be water-miscible or water-immiscible. Among the various materials which can be employed are those which form modified alkyd or polyester-type resins, styrene-divinylbenzene copolymers, and acrylamide and N,N'-methylene-bis-acrylamide copolymers, although these are not to be considered limiting.

Among the resin-forming materials which we can utilize are those affording modified polyester-type resins, and U.S. Patents Nos. 2,255,313, 2,443,735 and 2,443,741 give examples of these materials. The first of these patents describes resin-forming materials containing a resin which is a substantially linear polyhydric alcohol ester of an unsaturated polybasic acid material of the maleic type mixed with a liquid substituted-ethylene body of resin-forming characteristics which is copolymerizable and miscible with the resinous material, for instance a vinyl compound. Thus the resin or plastic obtained from this mixture can be the reaction product of a maleic-type polybasic acid, a polyhydric alcohol and a vinyl compound.

This patent lists a number of suitable reactants; for instance, the polybasic acid may be maleic anhydride, maleic acid, fumaric acid, etc. and the preferred acid materials contain a single double bond and up to about 5 carbon atoms. The polyhydric alcohols are preferably dihydric of the type which react with dibasic acids to yield linear molecules or linear polyesters. Various of the dihydric alcohols are listed in the patent, for instance diethylene glycol, ethylene glycol, triethylene glycol, propylene glycol, etc., and the preferred alcohols are the glycol and glycol ethers of up to about 12 carbon atoms. In the resin-forming material the polyester resin formed from the dibasic acid and the glycol is mixed with an ethylenic polymerizable body, preferably a vinyl compound such as vinyl esters, vinyl ethers, styrene, etc. The mixtures containing the polyester resin and ethylenic compound, for instance styrene, are sold commercially and additional styrene, a densifier a catalyst and a promoting material can be added to provide a composition which will be satisfactory as the resin-forming material in our invention.

U.S. Patent No. 2,443,735 describes a resin-forming material which includes a resin possessing a plurality of polymerizable reactive alpha, beta enal groups and at least one material containing the $\text{CH}_2=\text{C}<$ linkage. The resin component of this mixture is produced by the esterification of an alpha, beta unsaturated polycarboxylic acid with a polyhydric alcohol, such as a glycol, while the $\text{CH}_2=\text{C}<$ body can be, for instance, styrene. Thus, the ingredients of this resin-forming material can be generally the same as those described with reference to U.S. Patent No. 2,255,313. In Patent No. 2,443,741 similar resin-forming materials are disclosed. However, the $\text{CH}_2=\text{C}<$ body is of the polyallyl type, for instance a polyallyl ester, and a number of these are mentioned in this patent.

As a more specific example a resin-forming material suitable for our use is provided by mixing about 20 to 35% by volume of an unsaturated polyester resin of the type disclosed in these patents as a solution containing about 30 to 60% by volume of styrene; about 80 to 65% by volume of styrene; about 0.01 to 4% by volume of a promoter; about 0.01 to 3% by volume of a polymerization catalyst; and a sufficient amount of a densifier to adjust the specific gravity of the mixture within the range of about 1.07 to 1.18. The polyester resin component can be Laminac 4111, a polyethylene glycol maleate resin mixed with styrene. To adjust the specific gravity of the resin-forming mixture within the range of about 1.07 to 1.18, a chemically inert densifier can be added which has a low viscosity, for instance about 1 to 15 centipoises, preferably about 1 to 5, at 60° F.; and a specific gravity of over about 1.5; and which is water-insoluble and non-polymerizable. Among the preferred densifiers are included benzoyl chloride, dichlorobenzene and dinitrodi-phenyl. A particularly effective densifier is tetrabromoethane and generally the addition of about 3 to 6 volume percent of this material is advantageous.

In order to facilitate the polymerization reaction the addition of a small amount of a promoter, for example about 0.01 to 4 weight percent of cobalt naphthenate or dimethyl aniline, is preferred. Apparently, the promoter acts as a linking agent and in combination with the catalyst initiates a faster polymerization reaction at the relatively low polymerization temperatures encountered in a well bore. By varying the amount of promoter and catalyst the working life of the resin-forming material can be regulated. Among the promoters which can be employed in this invention are the organic acid salts of metals such as aluminum and calcium, for instance calcium stearate, aluminum stearate, aluminum naphthenate and calcium naphthenate.

The polymerization catalysts utilized to effect the copolymerization or condensation reactions between styrene and the modified polyester resin-styrene solution can be the organic peroxide catalysts such as benzoyl peroxide, methylethyl ketone peroxide, tetrabutyl hydroperoxide or

cyclohexanone peroxide. Particularly effective catalysts are a 60% solution of methylethyl ketone peroxide in dimethyl phthalate or benzoyl peroxide in a 50% mixture with tricresyl phosphate. As mentioned the working life of the resin-forming material is dependent upon the amounts of polymerization catalyst and promoter present as well as the temperature in the well bore, and generally polymerization starts immediately after the catalyst and promoter have been added. Consequently, at ambient temperatures within a well bore, for instance about 70 to 75° F., the amount of catalyst employed preferably is in the range of about 0.4 to 0.7% by volume of the resin-forming material which affords a working life of about 30 to 60 minutes. The amount of catalyst required to sustain the working life of the resin-forming material will increase as the temperature is decreased and thus at lower temperatures of about 50 to 60° F. the amount of catalyst employed may be as high as 3%.

Another resin-forming material which can be utilized in this invention is in an aqueous medium and has an initial viscosity approximating that of water. This material can be formed by dissolving a mixture of acrylamide and N,N'-methylene-bis-acrylamide in fresh water. Generally, this mixture contains about 1 to 25 weight percent of N,N'-methylene-bis-acrylamide and about 99 to 75 weight percent of acrylamide. The aqueous solution will usually include from about 5 weight percent of this mixture to its limit of solubility and preferably this amount is about 5 to 25%. Although the acrylamide as such is ordinarily used, its nitrogen atom could be substituted as with a hydroxy methyl or a hydroxy ethyl group. Ammonium persulfate is an acceptable catalyst to polymerize the aqueous mixture and it can be employed with a promoter such as sodium thiosulfate or nitrilo-tris-propionamide. The amounts of each of the catalyst and promoter usually are about 0.1 to 2 weight percent based on the aqueous solution of resin-forming material, and these amounts can be varied to give the desired working life. For instance, a weight ratio of catalyst to promoter of 1 to 2 in an aqueous solution containing 20 weight percent of the acrylamide and N,N'-methylene-bis-acrylamide (95% acrylamide and 5% N,N'-methylene-bis-acrylamide) will give a working life at 70° F. of about 60 to 120 minutes when the catalyst plus promoter is about 0.5 to 1.5% of the aqueous solution. A specific resin-forming material found useful contains 95 weight percent of acrylamide, 5 weight percent of N,N'-methylene-bis-acrylamide, 0.68 weight percent of sodium thiosulfate, 0.34 weight percent of ammonium persulfate, and the balance being water. The mixture has an initial viscosity (1.3 centipoises) approximating that of water (which is about 0.5 to 1.5 centipoises under the conditions in many well bores) and is not greater than about 2.0 centipoises over a working life of at least about 30 minutes to facilitate its placement in the permeable well area. The specific gravity of the mixture is about 1.12. The aqueous solution of amides can advantageously be used as the resin-forming material as it has a lesser tendency to emulsify in the well than do the modified polyester-type compositions.

A specific example of our method can be illustrated by reference to a field operation which is not to be considered limiting either procedurally or with respect to the composition of the resin-forming material. In this operation the well was a water flood injection well having a 1½" diameter cement tubing and a short bore hole. Three days were spent cleaning out the well by pumping water in and out of the bore hole using a ½" pipe wash string. An injection profile was obtained by the constant interface method using fresh and salt water and the well was found to be fractured at about 814½' from ground level. The total injection rate of the well was about 1 gallon per minute of fresh water at a well head pressure of 230 p.s.i.g. Five gallons of untriggered resin-forming material, composed of 65.3 parts by volume of

styrene, 28 parts by volume of Laminac 4111 and 4.6 parts by volume of tetrabromoethane, were passed down a ½" tubing which contained a conductivity profiling unit, see application Serial No. 618,583 to Stefan E. Szasz, filed October 26, 1956. The resin-forming material passed by the unit and emerged from the pipe or tubing piece extending from its lower end positioned at the interface between a lower layer of salt water and an overlying layer of fresh water which had been formed at about 814½' down the well. The resin-forming material was displaced down the ½" tubing at the rate of about 1 gallon per minute and while this was being done fresh water was bled at the well head from the annulus between the ½" tubing and the 1½" cement tubing. After all of the resin-forming material was in the ½" tubing a slug of salt water was added to provide a flush. During the charging of the resin-forming material into the ½" tubing string neither salt nor fresh water was added to the well. After the resin-forming material was placed in the salt-fresh water interface, the lower end of the profiling unit tubing was lowered into the salt water layer; and brine was then pumped down this tubing at the rate of 0.5 gallon per minute while fresh water was charged to the annulus between the ½" tubing and the 1½" cement tubing at the rate of 0.5 gallon per minute. By lowering and raising the profiling unit tubing, while ensuring that the bottom end of its lower tubing piece remained in the salt water level, the top of the resin-forming material layer was located at 814' while the bottom was at 815'. This determination was made immediately after the resin-forming material had been placed in the interface. This particular resin-forming material had a specific gravity of about 1.12 and was substantially non-conductive so that it could be distinguished from both the salt and fresh water layers by the use of the conductivity profiling instrument. Two minutes after the first check on the resin-forming material only about 0.1' of it could be located by the profiling unit and in less than 1 additional minute the material had been completely displaced or moved into the adjacent formation.

Shortly after the untriggered resin-forming material had been displaced into the adjacent formation, an essentially electrically, non-conductive mixture (5 gallons) containing the same amount of styrene, Laminac 4111 and tetrabromoethane and about 1.4 parts by volume of Nuodex (6% solution of cobalt naphthenate in mineral oil) and about 0.7 part by volume of Lupersol (60% methyl ethyl ketone peroxide in dimethyl phthalate), and having a specific gravity of about 1.12, was placed in the salt-fresh water interface by the procedure noted above except that the resin-forming material was flushed down the profiling unit tubing by fresh water. This composition had a working time of 20 to 30 minutes, i.e. time during which its viscosity is below about 15 centipoises at ambient temperature, and an initial viscosity of 8.3 centipoises at 70° F. Immediately upon the placing of the resin-forming material in the interface the profiling unit detected it at a position slightly above 814½', the location of the fracture. However, as the permeability of the well at locations other than the fracture was relatively low, the resin-forming material was displaced into the adjacent area through the fracture by continuing the fresh water and brine flows at the rate of 0.5 gallon per minute. After the mixing of the catalyst and promoter into the resin-forming material, it was in the fractured formation within about 10 to 15 minutes. The well was shut in for 45 minutes, that is the fresh and salt water brine flows were stopped about 15 minutes after the resin-forming material had left the well bore. Thereafter the injection rate of the well for fresh water was about 1 gallon per minute at a well head pressure of 350 p.s.i.g. so some plugging of the fracture had been effected.

To effect a more complete plugging an essentially electrically, non-conductive resin-forming mixture (5 gallons)

was formulated which contained equal amount of styrene and Laminac 4111 to provide 93.3 parts by volume, 4.6 parts by volume of tetrabromoethane, 1.4 parts by volume of Nuodex and 0.7 part by volume of Lupersol. After warming to 70 to 75° F. this resin-forming material was charged to the fresh-salt water interface in the manner described above within about 8.5 minutes after the catalyst and promoter had been mixed in the resinous composition. Immediately thereafter, the lower boundary of the layer of this material was located at approximately 814'. Fresh water flow was then started in the annulus between the profiling unit tubing and the 1½" cement casing to move the resin-forming material down the well and in 3½ minutes this material had been displaced from the well bore. 12.5 minutes after the mixing of the catalyst and promoter, the well was shut in for about 45 minutes. Fresh water injection to the well was then started down the annulus between the ½" and 1½" tubings and after 15 minutes the flow rate was 0.5 gallon per minute at a well head pressure of 375 p.s.i.g. The ½" tubing was pulled from the well as it has been plugged with approximately four gallons of resin-forming material. Nonetheless, it was found several days later that it required about 600 p.s.i.g. well head pressure to obtain an injection rate of water in the well of about 1 gallon per minute, and at a line pressure of 450 to 500 p.s.i.g. no substantial amount of water could be injected. Thus, the fracture located at 814½' had been effectively plugged and the well retained its capacity to receive water under moderate well head pressure.

In this invention there can be employed a special manner of placing the resin-forming material approximately adjacent the permeable well area when the material has viscosity characteristics generally similar to those of water under the temperature and pressure conditions of the well bore. There is described above a method for checking the location of the resin-forming material after it has been positioned in the salt water-fresh water interface which requires the raising and lowering of a conductivity profiling instrument from the layer of resin-forming material to the fresh and salt water columns. Thus, when the resin-forming material is essentially electrically non-conductive the conductivity profiling instrument will indicate distinct degrees of current flow when it enters the salt or fresh water layer on either side of the resin-forming material.

Although this procedure is feasible with certain resin-forming materials, difficulties in locating the materials can be experienced when their electrical conductivity characteristics do not differ sufficiently from those of both the fresh and salt water layers. To avoid this difficulty, a method has been devised for selectively plugging the permeable well area which method is based upon locating the salt-fresh water interface at a chosen level in the permeable area, to ensure that the resin-forming material is positioned approximately adjacent this area. Thus, by employing this procedure the chances of moving the resin-forming material into the well area at a location other than that desired are considerably reduced. In this method, the permeable area to be plugged is first located as to its vertical position in the well bore and the salt water-fresh water interface is provided at this area. The liquid organic resin-forming material is then positioned in the interface and moved into the adjacent permeable well bore wall and allowed to remain in this area of the formation to set up and provide a partial or complete plug. It is necessary that certain of these operations be restricted along given lines as will be pointed out.

In this method the resin-forming material is deposited, as from the lower end of a tubing, in or near, preferably in, the salt water-fresh water interface according to the procedures described above. The interface, however, is at a vertical position within the area to be plugged such that the upper and lower levels of the resin-forming material layer are, respectively, at the upper and lower boundaries of the area it is desired to plug at about the

same time. In order successfully to practice this method the permeability or injection profile of the overall sand face and of the permeable area to be plugged are determined at a plurality of vertical levels, for instance by one or both of the interface methods employing dissimilar liquids of essentially the same viscosity characteristics, such as fresh and salt water. Based upon these permeability measurements and the volume of the well bore adjacent the area to be plugged, the point of the fresh water-salt water interface within the permeable area is determined so that the resin-forming material will be positioned at the proper location. In this method the resin-forming material has essentially the same viscosity characteristics as the water layers between which it is placed, that is, a viscosity at 70° F. of about 0.5 to 2.0 centipoises, preferably about 1.0 to 1.5. The material retains these characteristics over a sufficient well life so that it can be moved into the permeable area before becoming materially more viscous. Preferably, the resin-forming material has an aqueous medium base and a specific gravity of about 1.07 to 1.18, advantageously about 1.11 to 1.13. The salt water layer employed preferably has a specific gravity of at least about 1.2. Unless the resin-forming material has a specific gravity of about 1.07 to 1.18, it should be deposited in the interface. Materials of this specific gravity can be deposited somewhat away from the interface as they tend to move through either the fresh or salt water towards the upper level of the salt water or the lower level of the fresh water. If, however, the material is deposited too far from the interface or permeable area, it may become unduly dispersed and go into the formation at undesired locations.

This method can best be described with reference to a specific example and the drawings; however, these are not to be considered limiting. In the drawings

FIGURE 1 shows an injection profile for the well and the well bore diameter at certain depths where it was shot;

FIGURE 2 is a diagrammatic illustration of the well during the injection of the resin-forming material;

FIGURE 3 is an illustration of the well undergoing the movement of the resin-forming material into the adjacent permeable area;

FIGURE 4 shows the water injection profiles of the well before and after the plugging treatment; and

FIGURE 5 shows the injection rate of the well before and after the plugging treatment over a range of well head pressures.

The injection profile of FIGURE 1, which plots percent cumulative injection rate versus well depth in feet, was determined by the salt water-fresh water constant interface method and this figure shows that the well bore diameter between 650 and 657" varied from about 13 to 22". The thief zone or permeable area to be plugged or treated was between about 652.5 and 655.5'. The well had about a 2" cement tubing in which was strung a ½" tubing for charging the resin-forming material. The total injection rate of the well at 315 p.s.i.g. well head pressure was 4 gallons per minute. In the plugging operation the resin-forming material was composed of:

	Percent
Acrylamide	19
N,N'-methylene-bis-acrylamide	1
Sodium thiosulfate	0.68
Ammonium persulfate	0.34
Water	Balance

and the material had the following properties at about 75° F.

Viscosity, centipoises	1.3
Specific gravity	1.12
Setting time, minutes	120

It is desired to locate the fresh water-salt water interface at a point A in FIGURE 2 which will result in the

upper interface between the fresh water and the resin-forming material being approximately at 652.5' (see point C of FIGURE 2) at about the same time that the lower interface between fresh water and resin-forming material is at about 655.5' (see point C₁ of FIGURE 2). This suitable location for the initial fresh water-salt water interface can be readily determined, and the resin-forming material is in this instance injected through tubing 10 having its lower end opening approximately in the interface. By an inspection of the injection characteristics of the thief zone or permeable area as illustrated in FIGURE 1, it is postulated that 655' might be about the proper position (A) for the fresh water-salt water interface. This can be checked by calculations.

In considering the travel of the upper interface between fresh water and resin-forming material during the latter's deposition in the bore, the injection characteristics

cross-sectional area of the portion of the bore involved is calculated. Thus

Area= $\frac{\pi D^2}{4}$ sq. ft.=1.305 sq. ft.

and the Δhu feet per minute=

$\frac{Vu}{\text{area}}=Vu \times \frac{1}{\text{area}}=0.353 \times 0.766=0.270$ feet per minute.

Thus, to raise the upper interface about 0.5' at this rate, it will take

$\Delta T \text{ minutes}=0.5' \times \frac{1 \text{ min.}}{0.270 \text{ foot}}=1.85 \text{ minutes.}$

These calculations can be made for each 0.5' interval until the upper interface is at about 652.5 feet. Data pertinent to these calculations are in the following table.

Table I

Interface Position, Feet	Δhu For Interval, Feet	Average Vu , Percent	Vu , Cu. Ft. per Min.	Bore Diam. (D), Feet	$\frac{1}{\text{Bore Area, Sq. Ft.}}$	Δhu , Ft./Min.	ΔT , Min.	Total T, Min.	Total Δhu
655.0	0	---	---	---	---	---	0	0	---
654.5	0.5	66	.353	1.292	.766	.270	1.85	1.85	0.50
654.0	0.5	61	.326	1.292	.766	.250	2.00	3.85	1.00
653.5	0.5	67	.305	1.250	.818	.250	2.00	5.85	1.50
653.0	0.5	46.3	.248	1.250	.818	.203	2.46	8.31	2.00
652.5	0.5	28.8	.154	1.125	1.009	.155	3.23	11.54	2.50

of the thief zone and its diameter show that the determination of the progress of the interface at 0.5 foot intervals should be suitable. Thus, the initial resin-forming material discharged from pipe 10 is at 655' and during the elevation of the upper interface to 654.5' the average percent of the total injection of liquid into the formation above 655' is about 66%, see FIGURE 1. As in this example, neither fresh nor salt water is entering the well during the positioning of the resin-forming material, the latter is entering at a total injection rate of about 4 gallons per mintue at 315 p.s.i.g. as the material has approxi-

The same calculations can be made for the travel of the lower interface between the resin-forming material and the salt water. Thus, for the initial 0.5' down from the brine-fresh water interface at 655'

$$\frac{V \text{ down (d) cu. ft.}}{\text{min.}}=\frac{Vd\%}{100} \times \frac{4 \text{ gal.}}{\text{min.}} \times \frac{.1337 \text{ cu. ft.}}{1 \text{ gal.}}$$
$$=\frac{28}{100} \times \frac{4}{1} \times \frac{.1337}{1}=0.150.$$

The other pertinent calculations are summarized in Table II.

Table II

Interface Position, Feet	Δhd For Interval, Feet	Average Vd , Percent	Vd , Cu. Ft. per Min.	Bore Diam. (D), Feet	$\frac{1}{\text{Bore Area, Sq. Ft.}}$	Δhd , Ft./Min.	ΔT , Min.	Total T, Min.	Total Δhd
655.0	0	---	---	---	---	---	0	0	---
655.5	0.5	28	.150	1.79	.397	.060	8.33	8.33	0.50
655.67	0.17	25	.134	1.79	.397	.053	3.21	11.54	0.67

mately the same viscosity and thus injection characteristics as the water used in establishing the injection profile of FIGURE 1. During the addition of the resin-forming material an aqueous medium could be added to one or both of the fresh and salt water layers to provide the total injection rate at the well head pressure employed where it is desired to add less of the resin-forming material than the total injection rate. However, this is not the preferred operation as these water flows would influence the movement of the upper and lower resin-forming material interfaces and these effects should be taken into consideration in figuring the arrival times of the upper and lower interfaces at the boundaries of the permeable area. In any event, since the rate of entry of the resin-forming material exceeds its rate of loss to the formation at the interface a layer of the material is formed between the fresh and salt water layers. Accordingly, the volume of resin-forming material added above the original level of 655' during the initial charging period (Vu) is

$$\frac{Vu \text{ cu. ft.}}{\text{min.}}=\frac{66}{100} \times \frac{4 \text{ gal.}}{\text{min.}} \times \frac{0.1337 \text{ cu. ft.}}{1 \text{ gal.}}=0.353$$

To determine the rate of the rise in height of the resin-forming material above the 655' level (Δhu), the average

The data of Tables I and II show that the upper interface should reach 652.5' in a resin-forming material charging period of about 11.54 minutes, while in this time the lower interface goes to about 655.67' which is only slightly below the lower boundary of the thief zone at 655.5'.

Thus, the selection of 655' for the initial salt water-fresh water interface will be sufficiently accurate in this method to obtain selective plugging of the thief zone with the upper and lower interfaces being respectively at the desired final positions at approximately the same time. If the initially chosen position for point A results in too much resin-forming material being opposite a non-thief area, then the calculations can be repeated at another initially assumed position until a satisfactory location for point A is determined.

In moving the resin-forming material into the permeable area adjacent the well bore there need not be an extraneous pressuring force exerted as the hydrostatic head of the fresh water column will push the material into the formation. However, we prefer that an aqueous medium be added either to the lower salt water layer after moving tubing 10 to the position shown in FIGURE 3 or to the upper fresh water layer by charging the aqueous medium to the annulus around tubing 10. Advantageously, how-

ever, aqueous medium is added to both of these layers simultaneously to squeeze the resin-forming material into the formation. Thus as shown in FIGURE 3, salt water is added to the salt water layer through the ½" tubing 10, and fresh water is added to the fresh water layer at the well head by charging to the annulus between the ½ and 2" tubings.

The desired location for the final fresh water-salt water interface can be indiscriminately chosen but the formation of the interface at a given location is readily accomplished. Thus by reference to FIGURE 1, this location can be designated, for instance 654', and to obtain the desired result fresh water is added to the upper layer at 58.8% of the total injection rate of 4 gallons per minute at 315 p.s.i.g. well head pressure and salt water is charged to the lower brine layer at 41.2% of the total injection rate. Calculations can be made to follow the upper and lower interfaces as they move towards the 654' point but these need not be illustrated here as the respective flows of fresh and salt water during squeezing have been chosen so that neither the upper nor the lower interface will go past the 654' mark regardless of whether or not they reach this point at the same time. After the resin-forming material is moved into the adjacent formation it is allowed to set by shutting in the well for an adequate time, for instance 2 hours.

This well was plugged by the method set forth immediately above. As the resin-forming material is precatalyzed by steel, all such surfaces which contacted the material were coated with an asphaltic composition and before the resin-forming material was charged to tubing 10, it was flushed with fresh water to remove salt. The results of this plugging operation are depicted in FIGURE 4 which shows the percent of water injection at various sand depths as determined by the constant interface method using fresh and salt water. Note that in the treating zone which originally took about 55% of the injected volume there was uniformly low injection after the plugging treatment. Also, the profile illustrates that a change in flow distribution was effected and there was a high permeable zone between 667 and 671'. This zone was accepting about 25% of the total injected water. However, in FIGURE 5, a plot of injection rate versus well head pressure shows that in order to obtain a volume of water injection to this permeable area comparable to that originally experienced in the zone treated between 650 and 660' a substantially higher well head pressure would have to be employed. Also, in subsequent water flooding procedures the passage of water through the high permeable area shown after the plugging treatment should effect substantial oil recovery before water breaks through to the output well. Nonetheless, after the break-through it may be desirable to plug selectively the permeable area which is shown at around 670'. This of course could be accomplished by the procedure described with reference to plugging the permeable area between 650 and 660'.

In the calculations made with reference to the travel of the upper and lower interfaces, certain analyses were on the assumption that variations in surface tension, wettability, density and viscosity between the various fluids are negligible in that the permeability of the sand in the immediate vicinity of the well bore does not change appreciably by the flow of any one of these three fluids. The efficacy of the plugging treatment illustrates that these assumptions are practically based.

We claim:

1. In a method for selectively decreasing the permeability of a permeable portion of a well area by plugging the permeable portion with a liquid organic resin-forming material, the steps comprising conducting an injectivity profile in the well by vertically traversing the well area with a primary interface formed between two dissimilar aqueous liquids, each of which can be distinguished by detection means, to locate the permeable portion to be plugged, said permeable portion being spaced upwardly

from the bottom of the well, forming a secondary interface between a salt water layer in the lower portion of the well and an overlying fresh water layer, adjusting the amounts of the respective liquids in the layers to position said secondary interface within said located permeable portion of the well, charging into said secondary interface an aqueous, liquid, organic resin-forming material having a specific gravity from about 1.07 to 1.18 and a viscosity of about 1 to 5 centipoises, said secondary interface being located within said permeable portion at a position determined from the injectivity profile such that the upper and lower levels of the material arrive at approximately the same time at the upper and lower levels of the permeable portion of the well to be plugged, displacing the resin-forming material into the adjacent permeable area, and allowing the resin-forming material to set and plug said permeable portion of the well.

2. The method of claim 1 in which the resin-forming material is an aqueous medium containing a mixture of acrylamide and N,N'-methylene bisacrylamide.

3. The method of claim 1 wherein the interface employed in conducting the injectivity profile is formed between a salt water layer and an overlying fresh water layer.

4. The method of claim 3 wherein the resin-forming material is an aqueous medium containing a mixture of acrylamide and N,N'-methylene bisacrylamide and after said resin-forming material is charged in the interface formed between the salt water layer and the overlying fresh water layer, an aqueous medium is added to at least one of said fresh water layer and said salt water layer.

5. The method of claim 1 wherein an aqueous medium is added to at least one of said fresh water layer and said salt water layer to displace the liquid organic resin-forming material into the permeable portion of the well area.

6. In a method for selectively decreasing the permeability of a permeable portion of a well area by plugging the permeable portion with a liquid organic resin-forming material, the steps comprising conducting an injectivity profile in the well by vertically traversing the well area with a primary interface formed between two dissimilar aqueous liquids, each of which can be distinguished by detection means, to locate the permeable portion to be plugged, said permeable portion being spaced upwardly from the bottom of the well, charging separate streams of salt and fresh water to the well to form a secondary interface between a salt water layer in the lower portion of the well and an overlying fresh water layer, adjusting the respective amounts of salt and fresh water to position the secondary interface within said located permeable portion of the well, stopping the flow of salt water to the well and charging the secondary interface with an aqueous, liquid organic resin-forming material having a specific gravity from about 1.07 to 1.18 and a viscosity of about 1 to 5 centipoises, said secondary interface being located within said permeable portion at a position such that the upper and lower levels of the material arrive at approximately the same time at the upper and lower levels of the permeable portion of the well bore to be plugged, displacing the resin-forming material into the permeable portion, and allowing the resin-forming material to set and plug said permeable portion of the well bore.

7. The method of claim 6 wherein the interface employed in conducting the injectivity profile is formed between a salt water layer and an overlying fresh water layer.

8. The method of claim 7 wherein the resin-forming material is an aqueous medium containing a mixture of acrylamide and N,N'-methylene bisacrylamide and after said resin-forming material is charged into the interface formed between the salt water layer and the overlying fresh water layer, an aqueous medium is added to at least one of said fresh water layer and said salt water layer.

9. In a method for selectively decreasing the perme-

ability of a permeable portion of a well area by plugging the permeable portion with a liquid organic resin-forming material, the steps comprising conducting an injectivity profile in the well by vertically traversing the well area with a primary interface formed between two dissimilar aqueous liquids, each of which can be distinguished by detection means, to locate the permeable portion to be plugged, said permeable portion being spaced upwardly from the bottom of the well, charging separate streams of salt and fresh water to the well to form a secondary interface between a salt-water layer in the lower portion of the well and an overlying fresh-water layer, adjusting the respective amounts of the salt and fresh water to position said interface within said located permeable portion of the well, stopping the flow of salt water and fresh water to the well and charging in the secondary interface an aqueous liquid resin-forming material having a specific gravity from about 1.07 to 1.18 and a viscosity of about 1 to 5 centipoises, said secondary salt water-fresh water interface being located within said permeable portion at a position such that the upper and lower levels of the material arrive at approximately the same time at the upper and lower levels of the portion of the well bore to be plugged, displacing the resin-forming material into the permeable portion of the well bore, and allowing the resin-forming material to set and plug said permeable portion of the well bore.

10. The method of claim 9 in which the resin-forming material is an aqueous medium containing a mixture of acrylamide and N,N'-methylene bisacrylamide.

11. The method of claim 9 wherein the interface employed in conducting the injectivity profile is formed between a salt water layer and an overlying fresh water layer.

12. The method of claim 11 wherein the resin-forming material is an aqueous medium containing a mixture of acrylamide and N,N'-methylene bisacrylamide and after said resin-forming material is charged into the interface formed between the salt water layer and the overlying fresh water layer, an aqueous medium is added to at least one of said fresh water layer and said salt water layer.

13. In a method for selectively decreasing the permeability of a permeable portion of a well area by plugging the permeable portion with a liquid organic resin-forming material, the steps comprising conducting an injectivity profile in the well by vertically traversing the well area with an interface formed between a salt water layer in the lower portion of the well and an overlying fresh water layer to locate the permeable portion to be plugged, said permeable portion being spaced upwardly from the bottom of the well, adjusting the amounts of the respective salt and fresh water to position said interface within said located permeable portion of the well, charging the said interface with an aqueous, liquid organic resin-forming material having a specific gravity from about 1.07 to 1.18 and a viscosity of about 1 to 5 centipoises, said interface being located within said permeable portion at a position determined from the injectivity profile such that the upper and lower levels of the resin-forming material arrive at approximately the same time at the upper and lower levels of a permeable portion of the well to be plugged, displacing the resin-forming material into the permeable portion, and allowing the resin-forming material to set and plug said permeable portion of the well.

14. The method of claim 13 in which the resin-forming material is an aqueous medium containing a mixture of acrylamide and N,N'-methylene bisacrylamide.

15. The method of claim 13 wherein an aqueous medium is added to at least one of said fresh water layer and salt water layer to displace the liquid organic resin-forming material into the permeable portion of the well area.

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