

May 10, 1966

N. D. SMITH, JR

3,250,330

PROCESS FOR TREATING EARTH FORMATIONS

Filed Oct. 31, 1963

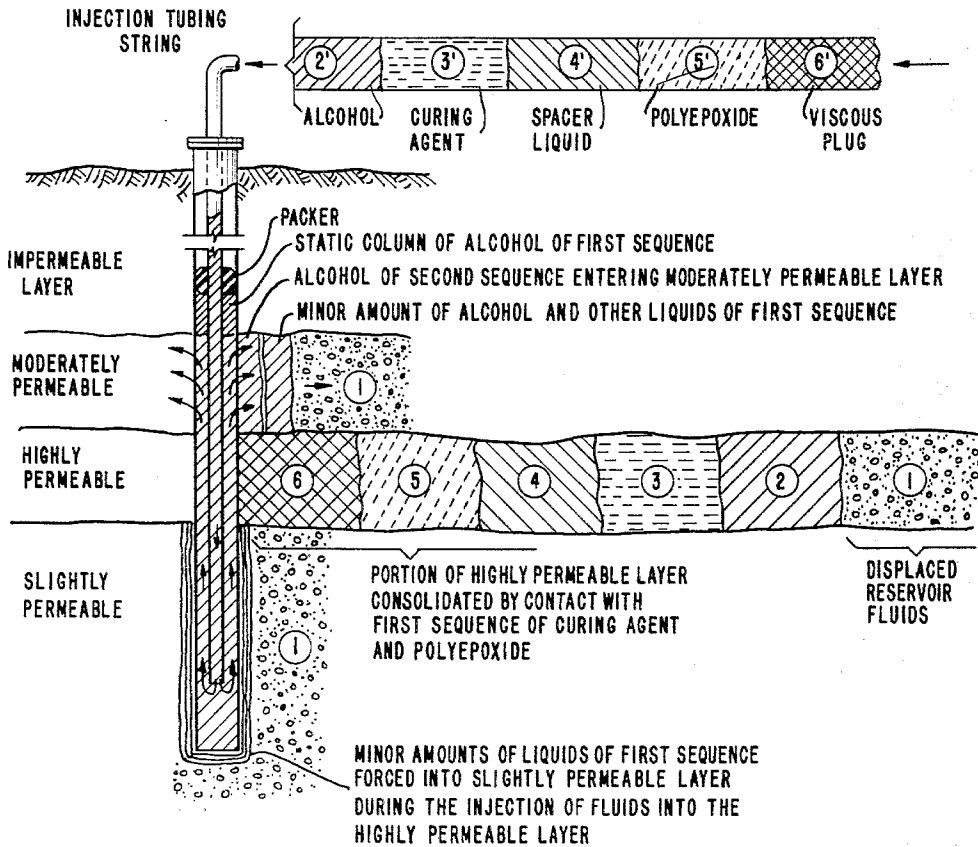
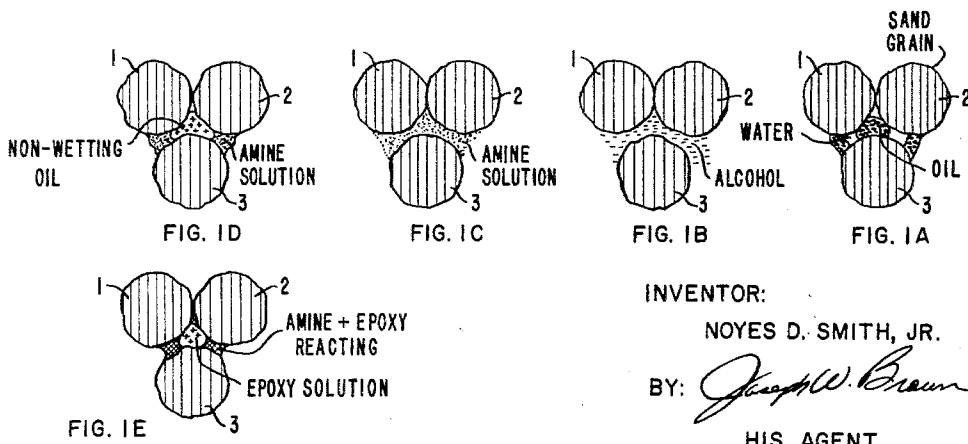


FIG. 2



INVENTOR:

NOYES D. SMITH, JR.

BY:

*Joseph W. Brown*

HIS AGENT

1

3,250,330

**PROCESS FOR TREATING EARTH FORMATIONS**  
Noyes D. Smith, Jr., Bellaire, Tex., assignor to Shell Oil  
Company, New York, N.Y., a corporation of Delaware  
Filed Oct. 31, 1963, Ser. No. 320,436  
16 Claims. (Cl. 166—33)

This invention relates to a process for treating earth formations. More particularly, the invention relates to a method for treating unconsolidated or substantially unconsolidated masses such as loose sand, particularly surrounding oil wells or water wells, while retaining a substantial degree of permeability for the said consolidated mass.

Specifically, the invention provides a new and efficient process for treating unconsolidated masses, which may be water-wetted, to form consolidated masses having a substantial degree of permeability to materials, such as oil or water. The process comprises treating the unconsolidated mass with liquid containing a compound possessing a plurality of amino hydrogen, then treating the mass with liquid containing a polyepoxide possessing more than one vic-epoxy group, retaining the resulting mixture in contact with the unconsolidated mass for a sufficient time to effect substantial cross-linking of the polyepoxide.

As a special embodiment, the invention provides a method for treating wells, such as oil or gas wells, wherein the producing formation consists of unconsolidated or substantially unconsolidated sand with the object of consolidating the sand in the formation yet allowing fluids to flow freely therethrough. This process comprises pumping into the casing string liquid containing an amino-containing compound, then pumping into the casing string a liquid containing a polyepoxide.

The presence of an unconsolidated formation immediately surrounding a well borehole creates a problem in respect to producing fluids from the formation. It is known that the small sized particles of an unconsolidated formation, which are entrained by the fluid passing out of the formation and into a production well communicating therewith, remain suspended in the fluid, causing increased abrasion of metal parts and necessitating frequent cleanouts of production equipment, such as pumps, separators, etc. Coarser particles entrained by the fluid flowing into the well are deposited on the bottom of the well, reducing the rate of production as the producing section of the well is plugged by the increasing mass of particles deposited therein. If the production rate becomes too low, the well has to be cleaned out before a new production cycle can begin. In some cases the particles enter the well in such great quantities that it is not possible to produce the well economically. These drawbacks can be overcome by consolidating the loose formation surrounding the well bore.

The problem of consolidating a sand by means of a plastic coating is complicated and difficult. The majority of the sands are water wet and their pores contain droplets of oil surrounded by the water which is in contact with the grains. The connate water in the sands is usually alkaline, and basic mineral materials, such as carbonates, often comprise a significant portion of whatever naturally occurring cementing materials exist between the grains of the sand. The unconsolidated sands are encountered at widely varying depths and exist at temperatures ranging from about 90° F. to 350° F. The variations in the depth of the sand, as well as the variations in the permeability, and the variations in the size of tubing strings installed in the well interact to create wide variations in the time involved in pumping a liquid from a surface location into a sand encountered by the well.

These problems impose difficulties which are troublesome in respect to the conventional plastic sand consoli-

2

ation treatment using resins of the phenolformaldehyde type. The resins of this type are formed by reacting formaldehyde or formalin with an aryl hydroxy compound, such as phenol or cresol, in the presence of a catalyst. Suitable catalysts comprise water soluble acids, or bases, or stannous chloride, or a mixture of stannous chloride and an acid. Where the reactants are to be injected as the components of a solution, the phenol and the formaldehyde must be partially reacted to form an oily liquid phase in which those reactants, the partially cured resin and the catalyst, are mutually soluble. It is difficult to render sand grains preferentially wetted by a liquid phase, unless the liquid phase contains a material having the properties of preferentially wetting the sand grains. The stannous chloride catalyst, to some extent, exhibits this advantage over the basic catalyst, but has the disadvantage of reacting with components of the sand and thus losing its catalytic effect. Pretreating the sand with acids often fails to remove all the reactive materials and also tends to dissolve naturally occurring cementing materials, thus increasing the amount of consolidation which is required.

It has been proposed to use epoxy resins in the consolidation of the sand particles. Techniques using the mixture of epoxy resins and curing agents have met with considerable success. However, it has been found that in certain formations, and particularly those which contain substantial amounts of clay, even these resins have not proved entirely satisfactory.

It is an object of the invention, therefore, to provide an improved process for treating porous earth formations. It is a further object of the invention to provide the process for treating unconsolidated earth formations to convert them to consolidated masses having a good degree of permeability. It is a further object to provide a process for treating water-wetted porous earth formulations surrounding a borehole so as to bind particles together with a resinous material. It is a further object to provide a process for first contacting an unconsolidated earth formation with a liquid that wets the grains with a compound containing amino hydrogen and then contacting the so-wetted grains with a liquid containing a polyepoxide that forms a resinous material substantially as soon as it contacts the compound containing amino hydrogen. It is a further object to provide a method for consolidating earth formations that contain an amount of clay that impedes their consolidation by other methods of cementing the grains together with a resin. It is a further object to provide a method for consolidating earth formation intervals that have layers having different fluid permeability. These and other objects of the invention will be apparent from the following detailed description thereof.

It has now been discovered that these and other objects may be accomplished by the process of the invention which comprises treating an unconsolidated earth formation with a liquid containing a compound having a plurality of amino hydrogen, then treating the earth formation with a liquid containing a polyepoxide having more than one vic-epoxy group. It has been unexpectedly found that by this special technique one can treat unconsolidated earth formations to convert them into consolidated masses having a high degree of porosity and the success of the treatment is not impaired by the presence of clay in proportions that impede consolidations that utilize other resin forming materials or the same resin forming materials applied by a different technique. The above-described process is particularly suited for the treatment of formations surrounding injection wells or production wells. It may also be used in consolidating formations surrounding mine shafts or in consolidating subsoil for filtration purposes. It has been demonstrated to be successful in consolidating sands containing up to 20% by weight or more of clay.

What happens within an individual pore space if an unconsolidated sand when treated according to the process of the present invention is illustrated in FIGURE 1 of the attached drawing.

FIGURE 2 shows a slug-plug treatment of an interval containing layers of a different permeability.

FIGURE A of drawing 1 illustrates the presence of a mixture of oil and water between sand particles 1, 2 and 3. After introduction of an alcohol slug as noted herein-after, the oil-water mixture between the sand particles is replaced by the alcohol (see FIGURE B of drawing 1). An introduction of a slug containing the amine curing agent then replaces the alcohol between the sand particles as noted in FIGURE C. The introduction of a non-wetting oil, such as diesel oil, then replaces a portion of the amine solution as in FIGURE D. The epoxy resin solution which is then introduced, enters between the sand particles and reacts with the remaining amine curing agent to form an insoluble infusible bond between the various sand particles (see FIGURE E) while still leaving space for passage of the oil through the formation.

The present process, of treating an unconsolidated earth formation by first contacting it with liquid containing an amino hydrogen curing agent and then contacting it with liquid containing a polyepoxide, provides advantages over other techniques of treating such formations with the same resin forming materials. If the formation is treated with a solution that contains both the epoxide and the curing agent, the rate of reaction and the concentration of the reactants must be correlated with the solvent properties, to delay polymer precipitation until the solution is in place within the formation, to cause precipitation within a reasonable time after the solution is in place, and to provide sufficient resin to bind the grains without providing enough resin to restrict the permeability of the formation. Since, in the present process, the reactants are not mixed until the sand grains have been coated with a layer of liquid in which the curing agent is contained, neither the rate nor the concentration of the reactants is critical in respect to either the attainment of strong bonds between the grains or the retention of high porosity within the consolidated formation. This is particularly advantageous in making it possible to utilize rapidly reactive, resin forming components that coat the grains with a substantially cured resin substantially as fast as the sequence of curing agent and epoxide containing liquids are pumped through the formation. If the formation is first contacted with liquid containing the epoxide and then contacted with liquid containing the curing agent, the disposition of the resin and the strength with which it is bonded to the grains of the formation is less advantageous than those obtained by the present process. The amino hydrogen curing agents are uniquely active, relative to other organic materials, in respect to their affinity for adsorption on sand grains. Sand grains have an affinity for the adsorption of a polar molecule. In a typical oil containing reservoir formation a typical pore space comprises an opening between the corners, or substantially spherical surfaces, of adjacent sand grains. The surfaces of the grains are usually coated with a layer of adsorbed water and the oil usually forms a discrete droplet surrounded by a continuous layer of water. Pumping a water and oil miscible liquid into such a pore tends to displace both the water and the oil. The extent to which the grain surfaces are wetted by such a liquid depends upon the affinity of the liquid for adsorption on sand grains. Since this affinity of a liquid containing the present amino hydrogen curing agents is significantly greater than that of a liquid containing an epoxide, the present process, of first introducing the curing agent, tends to more thoroughly wet the sand grains and ultimately, to more firmly consolidate the earth formation. See FIGURE 1.

The polyepoxides to be used in the process of the pres-

ent invention include those compounds possessing more than one vic-epoxy group, i.e., a



group. These polyepoxides may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted if desired with non-interfering substituents, such as halogen atoms, hydroxyl groups, ether radicals, and the like. They may also be monomeric or polymeric.

For clarity, many of the polyepoxides and particularly those of the polymeric type are described in terms of epoxy equivalent values. The meaning of this expression is described in U.S. 2,633,458. The polyepoxides used in the present process are those having an epoxy equivalent greater than 1.0.

Various examples of polyepoxides that may be used in the process of the invention are given in U.S. 2,633,458 and it is to be understood that so much of the disclosure of that patent relative to examples of polyepoxides is incorporated by reference into this specification.

Other examples include the epoxidized esters of the polyethylenically unsaturated monocarboxylic acids, such as epoxidized linseed, soybean, perilla, oiticica, tung, walnut and dehydrated castor oil, methyl linoleate, butyl linoleate, ethyl 9,12-octadecadienoate, butyl 9,12,15-octadecatrienoate, butyl eleostearate, monoglycerides of tung oil fatty acids, monoglycerides and soybean oil, sunflower, rapeseed, hempseed, sardine, cottonseed oil, and the like.

Another group of the epoxy-containing materials used in the process of the invention include the epoxidized esters of unsaturated monohydric alcohols and polycarboxylic acids, such as, for example, soybean oil, sunflower, rapeseed, hempseed, sardine, cottonseed oil, and the like.

Another group of the epoxy-containing materials used in the process of the invention include the epoxidized esters of unsaturated monohydric alcohols and polycarboxylic acid, such as, for example,

di(2,3-epoxybutyl)adipate,  
di(2,3-epoxybutyl)oxalate,  
di(2,3-epoxyhexyl)succinate,  
di(3,4-epoxybutyl)maleate,  
di(2,3-epoxyoctyl)pimelate,  
di(2,3-epoxybutyl)phthalate,  
di(2,3-epoxyoctyl)tetrahydrophthalate,  
di(4,5-epoxydodecyl)maleate,  
di(2,3-epoxybutyl)terephthalate,  
di(2,3-epoxypentyl)thiodipropionate,  
di(5,6-epoxytetradecyl)diphenyldicarboxylate,  
di(3,4-epoxyheptyl)sulfonyldibutyrate,  
tri(2,3-epoxy)1,2,4-butanetricarboxylate,  
di(5,6-epoxypentadecyl)tartarate,  
di(4,5-epoxytetradecyl)maleate,  
di(2,3-epoxybutyl)azelaate,  
di(3,4-epoxybutyl)citrate,  
di(5,6-epoxyoctyl)cyclohexane-1,3-dicarboxylate,  
di(4,5-epoxyoctadecyl)malonate.

Another group of the epoxy-containing materials include those epoxidized esters of unsaturated alcohols and unsaturated carboxylic acids, such as

2,3-epoxybutyl 3,4-epoxypentanoate;  
3,4-epoxyhexyl, 3,4-epoxypentanoate;  
3,4-epoxycyclohexyl 3,4-epoxycyclohexanoate;  
3,4-epoxycyclohexyl 4,5-epoxyoctanoate;  
2,3-epoxycyclohexyl methyl epoxycyclohexane carboxylate.

Still another group of the epoxy-containing materials include epoxidized derivatives of polyethylenically unsaturated polycarboxylic acids such as, for example,

5

dimethyl 8,9,12,13-diepoxyeicosanedioate;  
dibutyl 7,8,11,12-diepoxyoctadecanedioate;  
dioctyl 10,11-diethyl-8,9,12,13-diepoxy-eicosanedioate;  
dihexyl 6,7,10,11-diepoxyhexadecanedioate;  
didecyl 9-epoxy-ethyl-10,11-epoxyoctadecanedioate;  
dibutyl 3-butyl-3,4,5,6-diepoxyoctadecanedioate;  
dicyclohexyl 3,4,5,6-diepoxyoctadecanedioate;  
dibenzyl 1,2,4,5-diepoxyoctadecanedioate;  
and diethyl 5,6,10,11-diepoxyoctadecanedioate.

Still another group comprise the epoxidized polyesters obtained by reacting an unsaturated polyhydric alcohol and/or unsaturated polycarboxylic acid or anhydride groups, such as, for example, the polyester obtained by reacting 8,9,12,13-eicosanedienedioic acid with ethylene glycol, the polyester obtained by reacting diethylene glycol with 2-cyclohexene-1,4-dicarboxylic acid and the like, and mixtures thereof.

Still another group comprises the epoxidized polyethylenically unsaturated hydrocarbons, such as epoxidized 2,2-bis(2-cyclohexyl)propane, epoxidized vinyl cyclohexene and epoxidized dimer of cyclopentadiene.

Another group comprises the epoxidized polymers and copolymers of diolefins, such as butadiene. Examples of this include, among others, butadiene-acrylonitrile copolymers (Hycar rubbers), butadiene-styrene copolymers and the like.

The polyepoxides that are particularly preferred for use in the compositions of the invention are the glycidyl ethers and particularly the glycidyl ethers of polyhydric phenols and polyhydric alcohols. The glycidyl ethers of polyhydric phenols are obtained by reacting epichlorohydrin with the desired polyhydric phenols in the presence of alkali. Polyether A and Polyether B described in above-noted U.S. 2,633,458 are good examples of polyepoxides of this type. Other examples include the polyglycidyl ether of 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane (epoxy value of 0.45 eq./100 g. and melting point 85° C), polyglycidyl ether of 1,1,5,5-tetrakis(hydroxyphenyl)pentane (epoxy value 0.514 eq./100 g.) and the like and mixtures thereof.

Other examples of the glycidyl ethers include the glycidyl ethers of novolac resins which resins are obtained by condensing an aldehyde with phenol. A typical member of this class is the epoxy resin from a condensate of formaldehyde and 2,2-bis(4-hydroxyphenyl)propane novolac resin.

The glycidyl polyethers of polyhydric phenols obtained by condensing the polyhydric phenols with epichlorohydrin are also referred to as "ethoxylene" resins. See Chemical Week, vol. 69, page 27, for September 8, 1951.

Of particular value in the process of the invention are the polyepoxides containing only carbon, hydrogen, oxygen and halogen atoms.

The other materials to be used in the process of the invention comprise compounds which possess a plurality of amino hydrogen atoms, i.e., a plurality of



groups wherein N is an amino nitrogen. These include the aliphatic, cycloaliphatic, aromatic or cyclic amino as well as derivatives thereof as well as the derivatives still condensing the necessary amino hydrogen.

Examples of these materials include, among others, the aliphatic polyamines, such as, for example, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 1,4-aminobutane, 1,3-diaminobutane, hexamethylene diamine, 3-(n-isopropylamino)propylamine, N,N'-diethyl-1,3-propanediamine, hexapropylene heptamine, penta(1-methyl-propylene)hexamine, tetrabutylene pentamine, hexa-(1,1-dimethylethylene)-heptamine, di(1-methylbutylene)triamine, pentaamylhex-

6

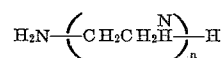
amine, tri(1,2,2-trimethylethylene)tetramine, tetra(1,3-dimethylpropylene)pentamine, penta-1,5-dimethylamyl-ene hexamine, penta-(1,2-dimethyl-1-isopropylethylene) hexamine and N,N'-dibutyl-1,6-hexanediamine.

Aliphatic polyamines coming under special consideration are the alkylene polyamines of the formula



wherein R is an alkylene radical, or a hydrocarbon-substituted alkylene radical, and n is an integer of at least one, there being no upper limit to the number of alkylene groups in the molecule.

Preferred aliphatic polyamines comprise the polyethylene polyamines of the formula



wherein n is an integer varying from about 2 to 8. Coming under special consideration are the polyethylene polyamines comprising 20-80% by weight of polyethylene polyamines having average molecular weights in the range of 200-500. These high molecular weight polyethylene polyamines normally start with tetraethylene pentamine and having related higher polymers which increase in complexity with increasing molecular weights. The remaining 80-20% of the mixture is diethylene triamine employed in such proportions that the mixture is fluid at about room temperature (60-90° F.).

Active nitrogen ----- 81%.  
Viscosity ----- 75-250 poises.  
Equivalent weight ----- 42.5 to 47.5%.

Other examples include the polyamines possessing cycloaliphatic ring or rings, such as, for example, 1-cyclohexylamino-3-aminopropane, 1,4-diaminocyclohexane, 1,3-diaminocyclopentane, di(aminocyclohexyl)methane, di(aminocyclohexyl)sulfone, 1,3-di(aminocyclohexyl)-propane, 4-isopropyl-1,2-diaminocyclohexane, 2,4-diaminocyclohexane, N,N'-diethyl-1,4-diaminocyclohexane, and the like. Preferred members of this group comprise those polyamines having at least one amino or alkyl-substituted amino group attached directly to a cycloaliphatic ring containing from 5 to 7 carbon atoms. These cycloaliphatic amines are preferably obtained by hydrogenating the corresponding aromatic amines. Thus di(aminocyclohexyl)methane is obtained by hydrogenating methylene dianiline.

Another group of materials that may be used in process of the invention comprise the organo-metallic compounds, such as those having a silicon or boron atom or atoms linked to amino or substituted amino groups. The compounds may also be those organo-metallic compounds wherein the amino groups or substituted amino group or groups are attached to carbon, such as in the alkoxycyclopropylamines as triethoxysilylpropylamines.

Still another group comprise the aminoalkyl-substituted aromatic compounds, such as, for example, di(aminoethyl)benzene, di(aminomethyl)benzene, tri(aminoethyl)benzene, tri(aminobutyl)-naphthalene and the like.

Still another group comprise the polymeric polyamines, such as may be obtained by polymerizing or copolymerizing unsaturated amines, such as allyl amine or diallyl amine, alone or with other ethylenically unsaturated compounds. Alternatively, such polymeric products may also be obtained by forming polymers or copolymers having groups reactive with amines, such as, for example, aldehyde groups, as present on acrolein and methacrolein polymers, and reacting these materials with monomeric amines to form the new polymeric polyamines. Still other polymeric amines can be formed by preparing polymers containing ester groups, such as, for example, a copolymer of octadene-1 and methyl acrylate, and then reacting this with a polyamine so as to effect an exchange of an ester group for an amide group and leave the other

amine group or groups free. Polymers of this type are described in U.S. 2,912,416.

Still other materials include the N-(aminoalkyl)piperazines, such as, for example, N-aminobutylpiperazine, N-aminoisopropyl-3-butoxypiperazine, N-aminoethylpiperazine, 2,5-dibutyl-N-aminoethylpiperazine, 2,5-dioctyl-N-aminoisobutylpiperazine and the like. Coming under special consideration are the N-(aminoalkyl)piperazines wherein the alkyl group in the aminoalkyl portion of the molecule contains no more than 6 carbon atoms, and the total molecule contains no more than 18 carbon atoms.

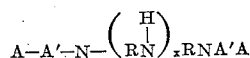
Coming under special consideration, particularly because of the better control over the rate of cure obtained, are the acetone soluble derivatives of the above polyamines as may be obtained by reacting the above-described polyamines with other materials to remove some but not all of the active amino hydrogen.

A group of such materials include those acetone soluble products obtained by reacting the polyamines with a monoepoxide. Examples of these reactants include, among others, ethylene oxide, propylene oxide, styrene oxide, phenyl glycidyl ether, allyl glycidyl ether, octadecyl glycidyl ether, tolyl glycidyl ether, chlorophenyl glycidyl ether, naphthyl glycidyl ether, diacetate of monoglycidyl ether of glycerol, dipropionate of the monoglycidyl ether of glycerol, epichlorohydrin, 1,2-decylene oxide, glycidyl acetate, glycidyl benzoate, glycidyl propionate, glycidyl acrylate, glycidyl methyl maleate, glycidyl stearate, glycidyl oleate, butyl 1,2-epoxypropionate and the like.

This reaction between the polyamines and monoepoxide is effected by merely bringing the components together in proper proportions. The adducts are obtained when a mole of the polyamine is reacted with not more than one mol of monoepoxide. The excess amine can be retained or removed by distillation. Examples of the monoepoxide-polyamine reaction products include, among others, N(hydroxypropyl) diethylene triamine (reaction product of propylene oxide and diethylene triamine) and N(2-hydroxy-4-phenoxypropyl) diethylene triamine (reaction product of phenyl glycidyl ether and diethylene triamine).

A group of related materials are those soluble fusible products obtained by reacting a polyepoxide with a monoamine. Examples of polyepoxides that may be used include any of those noted above for use in the compositions of the present invention. Examples of the monoamines include, among others, secondary amines as dimethylamine, diethylamine, dipropylamine, dibutylamine, di(tert-butyl)amine, dinonylamine, dicyclohexylamine, diallylamine, dibenzylamine, methyl ethylamine, ethylcyclohexylamine and the like. This reaction between the polyepoxides and monoamines is effected by merely bringing the components together in proper proportions. The desired soluble fusible products are obtained when the polyepoxide and monoamine are combined so as to have at least 1.5 mols of the amine per epoxide equivalent of the polyepoxide.

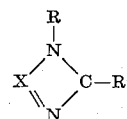
Another group of derivatives that may be used in the process of the invention include those soluble and fusible products obtained by reacting the polyamines noted above with unsaturated nitriles, such as, acrylonitrile. Examples of such products include the cyanoethylated diethylene triamine, cyanoethylated triethylene tetramine, cyanoethylated hexamethylene diamine, cyanoethylated 1,3-propanediamine and cyanoethylated 1,3-diaminocyclohexane. Preferred species of the cyanoalkylated polyamines include those of the formula



wherein x represents an integer in the range of 0 through 3 and A and A' represents a member selected from the group consisting of hydrogen and cyanoethyl radicals, and further characterized in that the amine has at least one

cyanoethyl group and at least one non-tertiary amino group in the molecule. Especially preferred members of this group comprise the cyanoethylated aliphatic and cycloaliphatic polyamines containing up to 18 carbon atoms.

Other suitable materials include the imidazoline compounds as prepared by reacting monocarboxylic acids with polyamines. These may be represented by the formula



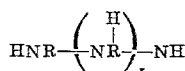
wherein X is an organic radical, and preferably an alkyl-ene radical, R' is a long chain hydrocarbon radical, and preferably one containing at least 12 carbon atoms, and R is an organic radical containing an amine or amine substituted group. Particularly preferred members of this group are those obtained by reacting any of the above-described polyamines with long chain monocarboxylic acids, such as those containing at least 12 and preferably 16 to 30 carbon atoms, such as, for example, palmitic acid, pentadecanoic acid, 4-ketomyristic acid, 8,10-dibromostearic acid, margaric acid, stearic acid, alpha-chlorostearic acid, linoleic acid, oleic acid, dihydroxystearic acid, arachidic acid, cluopanodonic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, melissic acid, and the like, and mixtures thereof. These imidazolines are prepared by heating the polyamine with the monocarboxylic acid and removing the water formed by the reaction. The acid and polyamine are combined in an equivalent ratio varying from about .3 to .7 to 1, and preferably about .3 to .5 to 1. The temperature employed preferably varies from about 100° C. to 250° C.

Still other examples include the sulfur and/or phosphorus-containing polyamines, such as may be obtained by reacting a mercaptan or phosphine containing active hydrogen with an epoxy halide to form a halohydrin, dehydrochlorinating and then reacting the resulting compound with a polyamine. N-(3-ethylthio-2-hydroxypropyl) diethylene triamine may be prepared, for example, by reacting ethyl mercaptan with epichlorohydrin, dehydrochlorinating and then reacting the resulting epoxy compound with diethylene triamine. Suitable examples of such compounds include, among others, N-(3-butylthio-2-hydroxypropyl) triethylene tetramine, N-(4-phenylthio-3-hydroxybutyl) pentamethylene tetramine, N-(4-cyclohexylthio-3-hydroxybutyl) ethylene diamine, N-(3-cyclohexylthio-2-hydroxypropyl) hexamethylene diamine, N-(3-diphenylphosphino-2-hydroxypropyl) triethylene tetramine, N-(3-dicyclohexylphosphino-2-hydroxypropyl) pentamethylene tetramine, N-(3-didodecylphosphino-3-hydroxyhexyl) diethylene triamine, and 3-(allylthio-2-hydroxypropyl) hexamethylene diamine. Coming under special consideration are the N(alkylthiohydroxyalkyl) aliphatic and aromatic polyamines, the N-(cycloalkylthiohydroxyalkyl) aliphatic and aromatic polyamines and the N-(arylthiohydroxyalkyl) aliphatic and aromatic polyamines. Preferred phosphorus-containing curing agents include the N-(dialkylphosphinohydroxyalkyl) aliphatic and aromatic polyamines, the N-(dicycloalkylphosphinohydroxyalkyl) aliphatic and aromatic polyamines, and the N-(diarylphosphinohydroxyalkyl) aliphatic and aromatic polyamines.

Still other derivatives that may be employed include those obtained by reacting the polyamines with acrylates, such as methyl acrylate, ethyl acrylate, methyl methacrylate and the like. In this case there is an exchange of the ester linkage for an amide linkage, one of the polyamine nitrogen being involved in the said amide linkage.

Particularly preferred polyamines and derivatives to be used with the above-described polyepoxides comprise

the aliphatic and cycloaliphatic polyamines of the formula



wherein  $x$  is an integer of 0 to 10 and  $R$  is a bivalent aliphatic or cycloaliphatic hydrocarbon radical containing from 1 to 10 carbon atoms, and derivatives obtained by reacting the aforescribed polyamine with monoepoxides containing from 2 to 10 carbon atoms, ethylenically unsaturated mononitriles containing 1 to 6 carbon atoms and monocarboxylic acids containing up to 20 carbon atoms.

Coming under special consideration, particularly because of the superior results obtained therewith, are the amino hydrogen-containing curing agents which are soluble in alcohol and insoluble in hydrocarbons such as toluene. Preferred examples of these include those which have alcohol soluble groups in addition to the amino hydrogen, such as  $-\text{OH}$  groups, sulfolanyl groups and the like. Examples include, among others,  $N(2,3\text{-dihydroxypropyl})$  diethylene triamine,  $N(\text{hydroxyethyl})$  diethylene triamine,  $N(2\text{-hydroxy-3-allyloxypropyl})$  diethylene triamine,  $N(\text{hydroxyethyl})$  ethylene diamine,  $N(\text{hydroxyethyl})$  triethylene tetramine and the like,  $N(3\text{-sulfolanyl})$  diethylenetriamine,  $N(3\text{-sulfolanyl})$  ethylenetriamine,  $N(3\text{-sulfolanyl})$  triethylene tetramine. Other examples of the hydroxy-containing polyamines can be found in Newey—U.S. 2,864,775, and examples of the sulfolanyl-substituted polyamines can be found in Newey—U.S. 3,041,352.

Accelerators may also be included with the solution containing the amino hydrogen containing material or with the solution containing the polyepoxide depending chiefly on their reactivity with these materials. Among the preferred accelerators are phenolic compounds, tertiary amines, mercaptans and the like. Particularly preferred are phenol and tri(dimethylaminomethyl)phenol. Other phenolic compounds, e.g., alkyl-substituted phenols, and the like may be used. The amount of these accelerators generally vary from about 0.1% to 5% by weight of the amine curing agent.

The proportions of the polyepoxide and the material having the amino hydrogen that are dissolved in the respective solution may vary within a wide range. The amount of the material possessing the amino hydrogen should be at least a 5% stoichiometric excess in respect to the polyepoxide with which it is reacted. As used herein and in the appended claims stoichiometric amount refers to that amount needed to furnish one amino hydrogen for every epoxy group to be reacted. Particularly superior results are obtained when the material containing the amino hydrogen is injected in the form of a substantially pure liquid or a relatively concentrated solution. In general as long as the solution containing the amino material is at least as concentrated as the solution containing the polyepoxide the amino material will be present in a suitable stoichiometric excess in the adsorbed layer on the grains of the earth formation, i.e., where the reaction occurs.

The polyepoxides and the amino-containing material are preferably employed in the process of the invention in the form of liquid solutions. If they themselves do not have the desired viscosity, they may be used in solution with solvents having the desired characteristics. Inert diluents that may be used include the liquid aliphatic, aromatic and cycloaliphatic hydrocarbons, mixtures thereof and mixtures with other materials, such as ketones, ethers, esters, halogenated hydrocarbons and the like. Examples of suitable solvents include, among others, aromatic xylenes, cyclohexane, cyclohexanone, alkanes from 5 to 10 carbon atoms, and the like and mixtures thereof. Other suitable aromatic hydrocarbons are those obtained by extraction of aromatics from kerosene, gas oil, spindle oil, lubricating oil or heavy catalytically cracked cycle

oil. A solvent particularly useful in respect to the liquid containing the polyepoxides for use in this invention is a kerosene extract boiling in the range from  $350^\circ$  to  $510^\circ$  F., e.g., an  $\text{SO}_2$  extract of kerosene having an API gravity of  $25\text{--}28^\circ$ , an initial boiling point between  $350$  and  $390^\circ$  F., an end point between  $450$  and  $510^\circ$  F. and an aromatic content of at least about 80% by weight, the remainder being saturated non-aromatic hydrocarbons. The hydrocarbon solution may be prepared from such aromatic solvent with admixture of hydrocarbon containing a greater proportion of non aromatics, e.g., unextracted kerosenes, gas oils or the like. In general, oils boiling above  $175^\circ$ , and preferably between  $350^\circ$  and  $650^\circ$  F. are employed as the polyepoxide solvents herein. Solvents particularly useful in respect to the liquid containing the amino hydrogen curing agent for use in this invention are the water and oil immiscible lower molecular weight alcohols, aldehydes, ketones, etc. such as ethanol, isopropanol, acetone, etc. Preferred solutions of either the polyepoxide or amino-hydrogen containing materials are those having viscosities between 1 and 100 centipoises at the temperature of the formation to be treated. Concentrations of the solutions as to the polyepoxide and amino hydrogen-containing material to obtain the desired fluidity generally varies from about 5 to 20% by volume.

According to the process of the invention, the solution containing the material possessing a plurality of amino hydrogen is first injected into the unconsolidated mass, and the mass is then treated with a liquid solution containing the polyepoxide. When the unconsolidated mass contains connate water, i.e., liquid water adhering to the grains due to capillary forces, and/or hydrocarbons such as oil such as may be the case in the underground sand formations, it is generally desirable to first remove such connate water and hydrocarbons before contacting the mass with the solution containing the amino hydrogen. Preferred technique for removing the water includes treatment of the mass with water-removing fluids, such as, for example, hydrocarbon-oxygen compounds having less than 6 carbon atoms per molecule and containing at least one keto-oxygen and/or hydroxyl group. Examples of such materials include, among others, isopropyl alcohol,  $n$ -propyl alcohol, sec butyl alcohol, acetone, methyl ethyl ketone and the like, and mixtures thereof. Usually the water and oil are adequately removed by the injection of a water and oil immiscible liquid such as a lower alcohol, but, in some cases, it is desirable to precede the alcohol slug with a slug of liquid hydrocarbon such as a slug of diesel oil.

If the water-removing compound is reactive with the compound containing the amino hydrogen, or with the polyepoxide, it is sometimes desirable to introduce a spacer fluid so as to prevent contact of the water-removing material with the reactants. The spacer fluid employed should preferably be mutually soluble with the water removing fluid in order to effectively drive water removing fluid containing connate water from the part of the mass to be consolidated. Suitable spacer fluids are, in general, hydrocarbons having the same composition as the hydrocarbons employed as solvents for the amino-containing material and the polyepoxide. Suitable spacer fluids include 10 to 90 parts of a kerosene extract having 80% aromatics made up to 100 parts with an essentially non-aromatic diesel oil.

In practicing the present invention, the preferred method is to first treat the unconsolidated mass with the water-removing solution. This may be accomplished by any suitable means, such as pumping, spraying, and the like. In the case of treatment of a well, the solution is pumped down through a string of tubing and into the loose formation to be consolidated. The liquid previously in the well is forced up through the annulus around the tubing string prior to setting a packer to force fluids pumped through the tubing to enter the earth formations.

In the next step, the spacer fluid or in most cases the



solution containing the amino hydrogen-containing compound is then applied to the unconsolidated mass by the same technique as noted above. The introduction of these solutions will tend to displace or remove the prior applied solutions to a great extent.

In the next step, the solution containing the polyepoxide is then applied to the unconsolidated mass by the above techniques as by pumping, spraying and the like. In the case of treatment of a well, the solution is pumped down the tubing string as with the other treating solutions. The introduction of this solution will tend to displace or remove a portion of the curing agent solution. However, the necessary amount of the curing agent will remain in the treated mass so as to effect a reaction with the polyepoxide.

In a preferred procedure, a spacer fluid which is a poor solvent for the amino hydrogen curing agent is applied between the application of the curing agent and the polyepoxide. The spacer fluid preferably consists essentially of relatively high molecular weight hydrocarbons such as those in a relatively light oil. The relatively light oils are particularly advantageous in that, relative to water and liquids containing the amino hydrogen curing agents, they are nonwetting liquids in respect to sand grains. The spacer fluid preferably has a viscosity of less than that of that amino hydrogen curing agent containing liquid and it is preferably displaced through the material containing the curing agent under conditions conducive to fingering, i.e., passing through the interstices between the individual grain of sand, so that it displaces the bulk of the liquid without removing the film of the curing-agent-containing liquid from the surface of the grains.

The mixture of the polyepoxide and curing agent is then allowed to remain in contact with the unconsolidated mass for a sufficient time to effect the necessary cross-linking reaction and consolidation of the unconsolidated particles.

After the necessary reaction has taken place, liquid is displaced through the mass to remove the solvents and/or unreacted polyepoxide or amino-hydrogen containing material. Examples of such include any of the above-described materials used in forming the solutions of the polyepoxides and amino-containing materials, such as hydrocarbons, as the aliphatic and aromatic hydrocarbons, cycloaliphatic hydrocarbons, esters, ketones, and the like, and mixtures thereof. If the well is an injection well, there can be used as a removing fluid a hydrocarbon such as a gas oil containing small amounts of aromatic compounds. If the well is to be used as a production well, the removing fluid in some cases can be constituted by the crude oil present in the formation, by merely bringing the well into production.

Because of the capability of utilizing curing agents and polyepoxides that react substantially instantaneously at the temperature of the formation being treated, the present process is particularly adapted for use in treating unconsolidated formation intervals that contain layers having different fluid permeability. The difficulties involved in said consolidations in such intervals are described in co-pending application Serial No. 169,016, filed January 26, 1962 now abandoned. In a typical process of treating such an interval, an injection tubing string is run through at least one packer disposed to seal the annulus around the string and isolate a section of the borehole so that fluids injected through the tubing string are forced to enter the isolated interval. A sequence of slugs of formation treating liquids, e.g., slugs of alcohol, liquid containing amino hydrogen curing agent, light oil, and liquid containing polyepoxide, are displaced in sequence through the tubing string and followed by a slug of a temporarily gelled viscous liquid. This first sequence of slugs is followed by at least one additional sequence, and the volume of each slug is made at least sufficient to completely fill the isolated section within the borehole. When the injection pressure is increased to a pressure exceeding that

of the fluids in the earth formation, fluids flow from the borehole into the most permeable layer adjacent to the packer isolated section of the borehole. By temporarily releasing the packer to permit the displacement of mud or well completion fluid from the packer-isolated section, this section is initially filled with the first slug, e.g., the alcohol, prior to injecting fluids into the earth formation. During the injection into the earth formation, the flow occurs within the borehole only along the most direct path from the opening in the tubing string to the most permeable layer of the formation, with the liquid in other portions of the packer-isolated section of the borehole remaining static. Since the alcohol slug is displaced by the curing agent slug, the trailing edge of the alcohol is followed by the leading edge of the curing agent, and the latter flows along the static portions of the alcohol and enters the permeable layer of earth formations immediately behind the alcohol. This movement past the static portions of alcohol and entry into the permeable layer is repeated in succession by the slugs containing the light oil and the polyepoxide. Portions of the curing agent are adsorbed on each grain of the formation and portions of the polyepoxide react to form a resin coating on those grains as the respective slugs flow through the permeable layer. The leading edge of the temporarily gelled viscous liquid similarly enters the permeable layer but, due to its temporarily high viscosity, increasing amounts of pressure are required to force it deeper into the formation. By the time all of the gelled liquid has been forced into the permeable layer the injection pressure has increased to one capable of forcing a less viscous liquid such as alcohol into a less permeable layer of the formation. In the next sequence of slugs of the alcohol, the curing agent, the light oil, and the polyepoxide enter and consolidate the layer of lesser permeability.

The use of the process of the invention in a slug-plug treatment of an interval containing layers of a different permeability is illustrated in FIGURE 2 of the attached drawing.

In an alternative process of using the present invention in a slug-plug treatment of an interval containing layers of different permeabilities, each of the treatment fluids are forced into each of the layers prior to the injection of the next fluid in the sequence of treating fluids. In this procedure the initial treating fluid, e.g., isopropanol, is spotted in the borehole, as described above. Then a sequence of slugs of the alcohol and a viscous but pumpable mixture of diesel oil thickened with aluminum soaps of organic acids is injected under incrementally increased injection pressures until the alcohol has entered all of the layers in the interval. After the alcohol and plugging material have remained in situ until the viscosity of the plugs have broken and reverted to a low viscosity, the next treatment fluid, e.g., a solution containing the curing agent, is similarly forced into all layers and allowed to remain, etc. In this procedure the gelled hydrocarbons, oil-in-water emulsions and the like types of essentially hydrocarbon plugging materials that revert to low viscosity liquids at the temperature of the subsurface earth formation are particularly preferred. Such substantially non-aqueous liquids have substantially no effects upon the reactions or products of the resin-forming components.

The capability of utilizing the rapidly reactive curing agents and polyepoxides also adapts the present process for use in wireline tool perforation and completions around the perforations in opening and consolidating one or a few adjacent perforations at a time. In such a wireline operation, the sequence of treating liquids are disposed in order in a chamber of a tool adapted to be lowered into a cased borehole and actuated for downhole operations by means of a wireline adapted to transmit electrical signals. The tool is actuated to perforate the casing, connect a conduit from the tool to the opening, and then inject the treating liquid slugs in sequence. When fast curing reactants are used, such an operation can feasibly be

performed with relatively short delays between the individual treatments.

#### Example I

A sandpack representative of an unconsolidated earth formation containing connate water and oil is prepared from clear Ottawa sand having particle sizes ranging from about 40–80 mesh. The sand is tamped into a glass tube to form a porous column having dimensions about 1 x 5". The column is maintained at room temperature (about 18° C.) in a vertical position and fluids are displaced through it by gravity drainage.

The sand is consolidated by contacting it in sequence with liquid slugs having volumes of approximately two pore volume (based on the pore volume of the sand column). The slugs comprise water, diesel oil a 20% by volume solution of 1,3-bis(aminoethylamino)-2-propanol in isopropanol, and a 20% by volume solution of a glycidyl polyether of 2,2-bis-(4-hydroxyphenyl)propane (polyether A described in U.S. 2,633,484) in an aromatic hydrocarbon solvent containing about 81% aromatics by volume and having a boiling temperature between 370° F. and 510° F. The flow of fluid through the sandpack is stopped with the polyepoxide solution in contact with the column and the column is allowed to stand overnight (about 16 hours). On the following day the residual polyepoxide solution is displaced with an approximately 2 pore volume slug of diesel oil.

This type of laboratory testing procedure is one which has been used many times in consolidations of similar sandpacks with solutions containing mixtures of the same types of polyamino hydrogen containing curing agents and polyepoxides. The diesel oil displacement of the unreacted liquid remaining in contact with the treated sandpack is indicative of the permeability of the treated pack. In a sand pack subjected to the presently described treatment the rate of flow of the diesel oil is indicative of the retention of a substantial portion, if not all, of the original permeability of the sandpack. The presently described treatment produces an integral porous cylinder of consolidated sand.

#### Example II

A sandpack representative of an unconsolidated earth formation composed of sand having a significantly high clay content is prepared by mixing a naturally occurring subsurface Gulf Coast miocene sand with bentonite clay to produce a mixture in which the crystalline components comprise 70% by weight alpha quartz, 20% by weight bentonite and 10% by weight feldspar.

This mixture is consolidated by tamping it into a tube, mounting it and treating it with a sequence of liquid slugs in the manner described in Example I. In this treatment the liquid slugs are identical with those described in Example I except for the omission of the initial water.

This type of treatment procedure is one which has been tried many times in testing the effects of solutions containing mixtures of polyamino hydrogen-containing curing agents and polyepoxides on sands having such a high content of clay. It has been demonstrated that the mixtures of these curing agents and polyepoxides consolidate a given sandpack to a far greater extent than are treatments utilizing the components of phenol formaldehyde or urea formaldehyde resins or treatments involving first injecting a liquid containing the polyepoxide and then injecting one containing the curing agent. Many tests of the effects of treating such a clay containing sand with solutions containing mixtures of various polyamino hydrogen curing agents and various polyepoxides, using various proportions of reactants, various temperatures, durations of treatments, etc., have consistently produced only crumbly, tacky, unconsolidated sandpacks.

In contrast the presently described treatment produces an integral porous cylinder of consolidated sand that re-

tains a substantial portion, if not all, of the original permeability of the sandpack.

#### Example III

An oil-producing well completed into an unconsolidated sand is prepared for treatment by installing a tubing string provided with packer means for isolating a section of the borehole that communicates with the sand and the interior of the tubing string as well as a mechanical plug catching means for catching a wiper plug that isolates a pair of successively injected liquids.

At the well site preparations are made for the sequential injection of at least two series of sequences of slugs of liquids containing, respectively, diesel oil, isopropanol, a 30% by volume solution of N-(hydroxyethyl)diethylenetriamine in isopropanol, a 20% by volume solution of a glycidyl polyether of 2,2-bis-(4-hydroxyphenyl)propane in an aromatic hydrocarbon solvent containing about 81% aromatics by volume and having a boiling temperature between 370° F. and 510° F. and a viscous but pumpable mixture of sodium borate, guar gum and sodium chloride in water. Except in respect to the viscous gelled liquid each of these slugs is arranged to have the volume at least equalling the volume of the packer isolated section of the borehole. The gelled liquid is arranged to have a volume such that when it is injected into the most permeable layer of the sand the pressure required for further fluid injection will be high enough to cause less viscous liquids to be injected into less permeable layers of the sand. The sequences of slugs are pumped through the tubing string and injected into the sand. During the initial stages of pumping the first alcohol slug, the packer is left unset so that the well completion fluids or other fluids in the borehole are displaced through the borehole annulus until the packer isolated section of the borehole is filled with alcohol. At this time the packer is set and the pumping pressure is increased to a pressure that exceeds the pressure of fluids in the formation to be treated but is less than the formation fracturing pressure. At each time the trailing edge of a slug containing the curing agent has entered the tubing string a mechanical wiper plug and a small amount of diesel oil (i.e., about the volume of the packer isolated section of the borehole) is inserted, to isolate that liquid from the liquid containing the epoxide until both of those liquids have been injected into the sand.

When the last epoxide containing slug has been injected into the sand, the well is shut-in. When sufficient time has elapsed to effect the curing of the resin and the breaking of the viscosity of the gelled liquid, the well is placed on production.

#### Example IV

Examples I, II, and III are repeated with the exception that the Polyether A is replaced with equivalent amounts of each of the following: diglycidyl ether of resorcinol, mixture of Polyether A and butyl glycidyl ether, mixture of Polyether A and phenylglycidyl ether, glycidyl ether of 2,4-di(2,3-epoxypropyl)phenol and a glycidyl ether of 1,1,2,2-tetrakis(hydroxyphenyl)ethane. Related results are obtained in each case.

#### Example V

Examples I to IV are repeated with the exception that the epoxy resin curing agent is replaced with equivalent amounts of each of the following: N-(2,3-dihydroxypropyl)diethylene triamine, N-(hydroxyethyl)triethylene tetramine, N-(2-hydroxy-3-allyloxypropyl)diethylene triamine, N-(3-sulfolanyl)diethylene triamine and N-(3-sulfolanyl)ethylene diamine. Related results are obtained in each case.

I claim as my invention:

1. A process for treating porous earth formations surrounding a borehole which comprises first injecting into the formation via the borehole a liquid containing an organic compound having a plurality of amino hydrogen



atoms, then treating the same previously treated formation via the borehole with a liquid containing a polyepoxide containing more than one vic-epoxy group so that there is contact between the compound containing the plurality of amino hydrogen atoms and the polyepoxide.

2. A process for consolidating an unconsolidated porous earth formation containing clay particles surrounding a borehole which comprises treating the formation by injection into the formation via the borehole a liquid solution containing a polyamine, then treating the same previously treated formation via the borehole with a liquid solution containing a polyepoxide so that the said polyamine comes in contact with the polyepoxide, and then subsequently displacing the unreacted polyamine and polyepoxide.

3. A process for treating a water-wet porous earth formation surrounding a borehole which comprises displacing all connate water from said formation, and then treating the earth formation via the borehole with a liquid solution containing a polyamine, and injecting a solution containing glycidyl polyether into the same previously treated formation via the borehole so that the said polyamine comes in contact with the polyepoxide and subsequently displacing the unreacted polyamine and unreacted glycidyl ether.

4. A process for treating porous earth formation surrounding a borehole comprising the steps of isolating a zone of said borehole adjacent to the formation to be treated, pumping a solution of a polyamine into said formation and through said isolated zone of said borehole, then pumping into said same previously treated formation a liquid solution of a polyepoxide, retaining said solution for sufficient time to permit partial cure of the epoxy resin and then producing the well.

5. A process for treating a water wetted earth formation penetrated by a borehole which comprises isolating a zone of said borehole adjacent to the formation to be treated, displacing substantially all connate water from the formation, pumping a solution of a polyamine into the formation through said isolated zone of said borehole, and then pumping into said same previously treated formation a liquid medium containing a polyepoxide, retaining said solution in said formation for sufficient time to permit partial cure of epoxy resin and then producing the well.

6. A process for treating a water-wetted earth formation penetrated by a borehole which comprises pumping into the earth formation to be consolidated via the borehole a water-removing solution, displacing that with a liquid containing a polyamine epoxy resin curing agent, then injecting into said earth formation a spacer fluid which is a poor solvent for the polyamine curing agent, then injecting into said earth formation a liquid medium containing a polyepoxide, retaining said solution in said earth formation for sufficient time to permit at least partial cure of the polyepoxide and then producing the well.

7. A process as in claim 6 wherein the water-removing solution is an alcohol.

8. A process as in claim 6 wherein the polyamine epoxy resin curing agent is an alcohol-soluble toluene-insoluble aliphatic polyamine containing no more than 30 carbon atoms.

9. A process as in claim 6 wherein the polyamine epoxy resin curing agent is 1,3-bis(aminoethylamino)2-propanol.

10. A process as in claim 6 wherein the polyamine epoxy resin curing agent is N-(hydroxyethyl)diethylenetriamine.

11. A process as in claim 6 wherein the polyamine epoxy curing agent is N-(3-sulfolanyl)diethylenetriamine.

12. A process as in claim 6 wherein the spacer fluid is an oil made up of relatively high molecular weight hydrocarbons.

13. A process as in claim 6 wherein the polyepoxide is a glycidyl polyether of 2,2-bis(4-hydroxyphenyl)propane.

14. A process as in claim 6 wherein the polyamine and polyepoxide are employed in an equivalent ratio varying from 1.2:1 to 2:1.

15. A process for treating an unconsolidated formation interval that contain layers having different fluid permeability which formation is penetrated by a borehole, which comprises running an injection tubing string through at least one packer disposed to seal the annulus around the string and isolate a section of the borehole, displacing in sequence through the tubing string slugs of alcohol, liquid containing an amino hydrogen containing curing agent, light oil and liquid containing polyepoxide, introducing a slug of a temporarily gelled viscous liquid, following this with a second sequence of slugs of alcohol, liquid containing an amino hydrogen-containing curing agent, light oil and liquid containing polyepoxide wherein the volume of each slug is made at least sufficient to completely fill the isolated section within the borehole, increasing the pressure so as to effect entry of the fluids into the various permeable layers, and after the polyepoxide has cured, releasing the packer and producing the well.

16. A process for treating an unconsolidated formation interval that contains layers having different fluid permeability which formation is penetrated by a borehole, which comprises running an injection tubing string through at least one packer disposed to seal the annulus around the string and isolate a section of the borehole, forcing into each of the layers a slug of polyamine and a plug of temporarily gelled viscous liquid as by varying the pressure, then forcing into each of the layers a slug of the polyepoxide by varying the pressure, and then after the temporarily gelled viscous liquid has broken and the polyamine and polyepoxide reacted, releasing the packer and producing the well.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

2,378,817	6/1945	Wrightsmen	166—33
2,604,172	7/1952	Wrightsmen	166—33
3,100,527	8/1963	Hilton et al.	166—33
3,123,137	3/1964	Young et al.	166—33
3,123,138	3/1964	Robichaux	166—33

CHARLES E. O'CONNELL, *Primary Examiner*.

BENJAMIN HERSH, *Examiner*.

S. J. NOVOSAD, *Assistant Examiner*.