METHOD OF STABILIZING PILES

BROADLY, the process of the present invention comprises stabilizing a structure embedded in an earth formation by disposing of a solidifiable liquid resin composition between at least an external portion of the structure and the surrounding earth formation, and solidifying the resin composition in intimate and static contact with both the structure and the formation, whereby the solidified resin is bonded to both the structure and the formation.

An important aspect of our new invention is the surprising discovery that when certain resin-forming polyepoxide compositions are flowed, as a liquid, from inside the piling into contact with a surrounding earth formation (especially a granular earth formation) and allowed to harden, the piling demonstrates a pull-out resistance materially exceeding that obtainable by methods hitherto known to those skilled in the art. Thus it is possible, as a result of our invention, to reduce both the number of piles necessary to form an adequate foundation and the depth to which such piles must be driven.

The prior art processes of anchoring pilings, such as by forming metal footings or by pouring slurries of concrete, or other cementitious materials around or from within the pile out into the surrounding earth, are subject to serious disadvantages which materially reduce the pull-out resistance of the piles when compared with those installed by our new process. Concrete and other aqueous liquid or slurry types of cementitious materials have definite infirmities which detract from their utility as stabilizing means for pile-like structures. For example, concrete or cement slurries are environment sensitive; thus, a fresh water cement slurry tends to flash-set and will not properly cure when flowed out into an incompetent earth formation comprising sea water, brine or the like. When attempts are made to flow cement slurries into such formations, it has been found that the slurry becomes deliquescent and forms an unpumpable mixture. Under such conditions, the sea water, etc., also causes the cement to become so diluted that its resistance to pull-out forces is very materially affected. The strength of cement or concrete is further diminished where the piles are desired to be secured against pull-out in clayey earth formations. This is due to the fact that the clay particles tend to absorb the water content from the cementitious mixture. This dehydrates the cement and causes voids which materially weaken the total cementitious structure, i.e., it becomes crumbly.

Where the soil into which the pile is driven is relatively permeable, the solid particles contained in the cementitious material will not flow out into the formation at all. Instead, the solids will filter out on the face of the formation and only the water content of the mixture will flow into the matrix of the formation. This tends to leave only a thin skin of dehydrated cement in the cavity formed by inserting the pile and such a situation does not materially increase the pull-out resistance of the pile. Furthermore, cement does not have a high bonding affinity for metal and tends to fracture at the point where it is joined to a metal pile when the latter is subjected to intense or shock-loading pull-out forces.

By using the preferred resin-forming compositions of our invention the aforementioned disadvantages of prior art metal footings or cementitious projections are overcome. The compositions of our invention comprise pumpable, oil-phase liquid mixtures which are not affected by water, i.e., they will not dehydrate or dilute and become an unpumpable mass, as will concrete or cement. Further, our preferred liquid compositions solidify at production rates in contact with sea water and other aqueous solutions which materially affect the curing or setting of cement. Also, the curing of our liquid mix compositions is unaffected by clayey particles which, as previously discussed, weaken cementitious mixtures and cause them to
become crumbly. This is because the liquid mix of our invention comprises a resin which will cure to form an extremely strong bond between the mix and any type of solid material, including clayey soil.

In addition, the preferred liquid mix of our invention may be used to stabilize piles in relatively permeable formations, where prior art cementitious materials are not effective because the suspended solid particles which, in such prior art mixtures, are essential to the formation of a solid grout, filter out on the face of the formation. Since our preferred mix is a solid free, pumpable, oil-phase liquid, the mix cures to a solid whether it is disposed within or adjacent to the matrix of the earth formation and thus it can be cured in either sandy formations or in relatively impermeable formations.

Furthermore, the preferred liquid mix of our invention will adhere to wet surfaces and solidify to form a much stronger bond to the metal pilings and to the earth formations than any material previously known. Tests have shown that under identical conditions our mix exhibited a shear strength of from at least 2 to 8 times as great as that for cementitious compositions. Finally, the solidified resin composition of our invention is elastic rather than brittle and resists shock better than concrete.

In general a liquid mix suitable for use in our invention basically comprises a resin-forming material capable of solidifying after injection into the earth. A preferred and especially suitable class of materials is that consisting essentially of a polyepoxide and a suitable curing agent, as further described hereinafter.

POLYEPOXIDES

The polyepoxides eminently suitable for use in the process of the present invention include those compounds possessing more than one vic-epoxy group, i.e., a

\[ \text{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. Patent No. 2,633,458. The polyepoxides used in the present process are those having an epoxy equivalency greater than 1.0.

Various examples of polyepoxides that may be used in the process of the invention are given in the said patent, 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 of 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,

- 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-epoxybutyl) tetrahydrophthalate,
- di(2,3-epoxydodecyl) maleate,
- di(2,3-epoxybutyl) terephthalate,
- di(2,3-epoxypentyl) thiodipropionate,
- di(5,6-epoxytetradecyl) diphenyldicarboxylate,
- di(3,4-epoxypentyl) sulfonypivalurate,
- tri(2,3-epoxybutyl)-1,2,3-butanetricarboxylate,
- di(5,6-epoxypentadecyl) tartarate,
- di(4,5-epoxytetradecyl) maleate,
- di(2,3-epoxybutyl) azelate,
- 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-epoxypanoate; 3,4-epoxyhexyl, 3,4-epoxypanoate;
- 3,4-epoxyhexyl, 3,4-epoxyoctadecene-1,2,3-carboxylate.

Still another group of the epoxy-containing materials include epoxidized derivatives of polyethylenically unsaturated polycarboxylic acids 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-epoxybutyl) tetrahydrophthalate; di(2,3-epoxydodecyl) maleate; di(2,3-epoxybutyl) terephthalate; di(2,3-epoxypentyl) thiodipropionate; di(5,6-epoxytetradecyl) diphenyldicarboxylate; di(3,4-epoxypentyl) sulfonypivalurate; tri(2,3-epoxybutyl)-1,2,3-butanetricarboxylate; di(5,6-epoxypentadecyl) tartarate; di(4,5-epoxytetradecyl) maleate; di(2,3-epoxybutyl) azelate; di(3,4-epoxybutyl) citrate; di(5,6-epoxyoctyl) cyclohexane-1,3-dicarboxylate; di(4,5-epoxyoctadecyl) malonate.

Still another group comprises the epoxidized polyethylene obtained by reacting an unsaturated polyalcohol and/or unsaturated polycarboxylic acid or anhydride groups, such as, for example, the polyester obtained by reacting 8,9,12,13-dieicosadienoic acid with ethylene glycol, the polyester obtained by reacting diethyleneglycol 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-cyclohexenyl) propane, epoxidized vinyl cyclohexene and epoxidized dimethylcyclopentadiene.

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 patent U.S. 2,633,458 are good examples of polyepoxides of this type. Other examples include the polyglycidyl ether of 1,2,5,6-tetraakis(4-hydroxyphenyl)ethane (epoxy value 0.45 eq./100 g. and melting point 85°C), polyglycidyl ether of 1,2,5,6-tetraakis(4-hydroxyphenyl)pentane (epoxy value 0.514 eq./100 g.) and the like and mixtures thereof.

The preparation of a glycidyl polyether of a dihydric phenol will be illustrated below. Unless otherwise specified, parts indicated are by weight.

PREPARATION OF POLYETHER A

1 mol of bis-phenol was dissolved in 10 mols of epichlorohydrin and 1 to 2% water added to the resulting
mixture. 5% by weight phenol was added to the mixture. The combined mixture was then placed in a kettle provided with heating and cooling means, agitator, distillation condenser and receiver. The mixture was brought to 80°C and 2 mols of solid sodium hydroxide added in small portions. Sufficient cooling is applied during the addition so that the temperature is maintained at about 95-100°C and there is a gentle distillation of epichlorohydrin and water. After the last addition of sodium hydroxide with the completion of the reaction, the excess epichlorohydrin is removed by vacuum distillation. After completion of the distillation, the residue is cooled to about 90°C and about 300 parts of benzene added. Cooling drops the temperature of the mixture to about 40°C with precipitation of salt from the solution. The salt is removed by filtration and the removed salt carefully washed with about an additional 300 parts of benzene to remove polymer therefrom. The two benzene solutions were combined and distilled to separate the benzene. When the ketone temperatures reached 125°C, vacuum is applied and distillation. The resulting product is a liquid composition containing glycidyl polymer of bisphenol having the following properties: epoxy value of 0.541 eq./100 g, color 6 (Gardner), chlorine (% weight) 0.24, viscosity 70 poises.

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 polymers 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 Sept. 8, 1951.

CURING AGENTS

The curing agents to be combined with the above-described polyepoxides in the process of the present invention comprise compounds which possess a plurality of active hydrogen atoms, such as are present in polyamines, polyamides, etc. The polyamines are those which possess a plurality of

\[ \underset{N}{H} - \underset{N}{H} \]

groups wherein N is an amino nitrogen. These include the aliphatic, cycloaliphatic, aromatic or cyclic amino as well as derivatives thereof including derivatives obtained by 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-propen diamine, hexapropylene diamine, penta(1-methylenepropylene)hexamine, tetra- butylene pentamine, hexa- (1,1-dimethylethylenetri) heptamido, di(1-methylethylene)trimethylpentamine, pentaamylhexamine, tri(1,2,2-trimethylethylenetetramine, tetra(1,3-dimethylpropylene)-pentamine, penta-1,5(dimethylamylene)hexamine, penta(1,2-1,3-dimethyl-1-isopropylpropylene)hexamine and N,N'-dibutyl-1,6-hexanediamine.

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

\[ \text{H}_2\text{N}(\text{RNH})_n\text{H} \]

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.
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 monooxide. Examples of these reactants include, among others, ethylene oxide, propylene oxide, styrene oxide, phenyl glycidyl ether, allyl glycidyl ether, octenyl glycidyl ether, naphthyl glycidyl ether, dicetate of monoglycidyl ether of glycerol, dipropionate of the monoglycidyl ether of glycerol, epichlorohydrin, 1,2-decylene oxide, glycidyl acetate, glycidyl benzole, glycidyl propionate, glycidyl acrylate, glycidyl methyl maleate, glycidyl stearate, glycidyl oleate, butyl 1,2-epoxypropionate and the like.

This reaction between the polyamines and monooxide is effected by merely bringing the components together in proper proportions. The additives are obtained when a mole of the polyamine is reacted with not more than the equivalent weight of monooxide. The excess amine can be retained or recovered 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-phenoxypyrolyl) diethylene triamine (reaction with ethylene glycol, or preferably one containing at least 12 carbon atoms, and R is an organic radical containing an amino or amine substituted group. Particularly preferred members of this group are those obtained by reacting any of the above-described polyamines with lone 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-ketomethylstearic acid, margaric acid, stearic acid, oleic acid, linoleic acid, oleic acid, dihydroxyacetic acid, arachidic acid, clupanodonic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, meissic 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 0.3 to 0.7 to 1, and preferably about 0.3 to 0.5 to 1. The temperature employed preferably varies from about 100°C to 250°C.

Other examples include the sulfur and/or phosphorus-containing polyamines, such as may be obtained by reacting a mercapto or phosphine containing active hydrogen with an epoxy halide to form a halohydrid, 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 mercaptoacrylonitrile and dehydrochlorinating and then reacting the resulting epoxy compound with diethylene triamine. Suitable examples of such compounds include, among others, N-(3-butilthio-2-hydroxypropyl) triethylene tetramine, N-(4-phenylthio-3-hydroxybutyl) pentamethylenetetramine, N-(4-cyclohexylthio-3-hydroxybutyl) ethylenediamine, N-(3-cyclohexylthio-2-hydroxypropyl) hexamethylenediamine, N-(3-diphenylphosphinophenoxypropyl) triethylene tetramine, N-(3-dicyclohexylphosphino-2-hydroxypropyl) pentamethylenetetramine, N-(3-didodecythio-3-hydroxyhexyl) diethylene triamine, and 3-(allylthio-2-hydroxypropyl)hexamethylenediamine. Coming under special consideration are the N-(allylthiodydroxalkyl) aliphatic and aromatic polyamines, the N-(cycloalkylthiohydroxalkyl) aliphatic and aromatic polyamines and the N-arylthiodydroxalkyl aliphatic and aromatic polyamines. Preferred polyamines containing curing agents include the N-(diarylpentaphos- phinoxyalkyl) aliphatic and aromatic polyamines, the N-(diarylcyclohexylphosphinoxyalkyl) aliphatic and aromatic polyamines, and the N-(diarylpentaphosphino- oxyalkyl) 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 polyamines comprise the aliphatic and cycloaliphatic polyamines of the formula

\[
\text{HNR}_2-\overset{\text{N}}{\text{H}}-\overset{\text{N}}{\text{H}}-
\]

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 aforesaid polyamines with monocarboxylic acids containing from 2 to 10 carbon atoms, hydroxy 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 hydrocarbon-containing curatives soluble in alcohol and insoluble in hydrocarbons such as toluene. Preferred examples of these include those which have
3,324,665 alcohol soluble groups in addition to the amino hydrogen, such as —OH groups, sulfonlany groups and the like. Examples include, among others, N(2,3-dihydroxypropyl) diethy1enetriamine, \( N(\text{hydroxyl})\text{diethylenetriamine}, \) (2-hydroxy-3-alloxypropy1) diethy1enetriamine, \( N(\text{hydroxyethyl})\text{ethylene diamine, } N(\text{hydroxyethyl})\text{triethylene tetramine and the like, } N(3-sulfonlany)\text{diethylenetriamine, } N(3-sulfonlany)\text{ethylenetriamine, } N(3-sulfonlany)\text{triethylene tetramine. Other examples of the hydroxy-containing polyamides can be found in the patent to Newey, U.S. 2,864,775, and examples of the sulfonlany-substituted polyamides can be found in the Newey patent, U.S. 3,041,352. Also preferred as curing agents are the polyamides. The polyamides used in the process of the invention comprise the reaction product of an aliphatic or cycloaliphatic polyalcoholic polycarboxylic acid containing at least 7 carbon atoms between the acidic groups, and an aliphatic polyamine, the resulting product possessing a group reactive with epoxy groups, such as, for example, free amino groups or free carboxyl groups.

Examples of polybasic acid materials used in making these polyamides include, among others, 1,10-decanediocid acid, 1,12 -dodecadiocid acid, 1,20 -eicosadiocid acid, 1,14-tetradecadiocid acid, 1,18-octadecadiocid acid and dimerized and trimerized unsaturated fatty acids obtained by heating polymerizing drying oil fatty acids under known conditions. Normally, this is effected by utilizing the larger aliphatic esters of drying oil esters so as to prevent decaerboxylation during the heating period. During the heating period, dimers and trimers are usually obtained. The process is illustrated in the "Industrial and Engineering Chemistry," vol. 38, page 1139 (1946). The structures of the products so obtained are believed to be those given in "Industrial Engineering Chemistry," vol. 33, page 89 (1941). Numerous drying oil acids can be used in preparing the polymerized acids, but the preferred acids are those containing from 16 to 24 carbon atoms, such as, for example, linoleic acid, linolenic acid, eleostearic acid, and linic acid, such as may be derived from oils, such as soybean oil, linseed oil, tung oil, perilla, oiticica, cottonseed, corn, tall, sunflower, dehydrated castor oil and the like. The expression "polymerized unsaturated fatty acids" as used herein in a generic sense is intended to include the polymerized mixture of dimerized acids, trimerized acids, higher polymerized acids as well as small portions of remaining monomers.

The aliphatic polyamides used in preparing the polyamides may be any di-, tri- or polyamine such as, for example, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 1,4-diaminobutane, 1,3-diaminobutane, hexamethylene diamine, 3-(N,N-isopropylamino)propy1amine, and the like. Particularly preferred polyamides are those containing from 2 to 12 carbon atoms, and especially those of the formula

\[
H_2NN\bigg(\begin{array}{c}
H \\
R \\
R
\end{array}\bigg)\bigg(\begin{array}{c}
H \\
R \\
R
\end{array}\bigg)
\]

where \( R \) is an integer of 0 to 10 and \( R \) is a bivalent hydrocarbon radical containing from 1 to 10 carbon atoms. Compounds of special consideration are those polyamines having at least 3 atoms intervening between the amine groups principally involved in the amidification reaction. These three atoms may be carbon atoms or hetero atoms, such as nitrogen atoms.

Especially preferred polyamides are those derived from the aliphatic polyamines containing no more than 12 carbon atoms and polymeric fatty acids obtained by dimerizing and trimerizing ethylenically unsaturated fatty acids containing up to 24 carbon atoms. These preferred polyamides have a viscosity between 10 and 1750 poises at 40° C, and preferably 20 to 250 poises at 40° C. Preferred polyamides also have amine values between 50 and 450. Amine number is number of milligrams of KOH equivalent to the free amino groups present in one gram of the polyamide.

Coming under special consideration are the fluid polyamides produced by the condensation of polymerized oleic acid with an aliphatic polyamine, e.g., diethylene triamine, and having the following properties: amine value 210-230, a viscosity of 500-750 poises at 40° C, specific gravity of 0.99 and weighing about 8.3 pounds per gram.

The polyamides used in the process of the invention preferably possess at least one and more preferably two or more hydrogen atoms attached to the amino nitrogen atoms or carboxyl hydrogen atoms. Such products are obtained by controlling the proportion of reactants so that there is always at least one amino hydrogen or carboxyl group, such as, for example, by using an excess of the polyamine reactant. A process for making such polyamides (to obtain free amino groups) or an excess of acid (to obtain carboxyl groups) is illustrated in U.S. 2,450,940 and U.S. 2,693,908 and so much of these patents relative to the preparation of the polyamides is incorporated herein by reference.

Accelerators may also be included with the solution containing the active hydrogen containing material or with the solution containing the polyepoxide described above, but essentially acting chiefly on their reactivity with these material. Among the preferred accelerators are phenolic compounds, tertiary amines, mercaptans and the like. Particularly preferred are phenol and tri-(dimethy1aminomethyl)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 epoxide 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 adhesively cured layer on the grains of the earth formation, i.e., where the reaction occurs.

The polypeoxides and the amino-containing materials 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 hydrocarbons such as benzene, 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 the liquid containing the polyepoxides for use in this invention is a kerosene extract boiling in the range from 350° to 510° F., e.g., an SO2 extract of kerosene having an API gravity of 25-28°, an initial boiling point between 350 and 390° F., and end point between 450 and 510° 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 aro-
matic 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°, and preferably between 350° and 650° F. and containing 50% or more of the polyolze solvent solvents herein. Solvents particularly useful in respect to the liquid containing the amino hydrocarbon curing agent for use in this invention are the water and oil immiscible lower molecular weight alcohol, aldehydes, ketones, etc. such as ethanol, isopropanol, acetone, etc. Preferred solutions of either the polyolze or amino-hydrocarbon 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 polyolze and amino hydrocarbon containing material to obtain the desired fluidity generally varies from about 5 to 20% by volume.

To illustrate the manner in which the liquid mix of the invention may be prepared, the following example is given. It is to be understood, however, that the example is for the purpose of illustration and the invention is not to be regarded as limited to any of the specific materials or conditions recited therein.

**Example**

This example illustrates the preparation of a liquid mix containing Polyether A and a polyamide of dimixed linoleic acid and diethylene triamine.

The composition was prepared by mixing the following components together in the proportions shown:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Polyamide of dimixed linoleic acid and diethylene triamine amine having an amine value of 306</th>
<th>Polyether A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

The method of the invention and further advantages thereof will be better understood from the following description taken with reference to the accompanying drawings wherein:

FIGURE 1 is a schematic elevation, partially in longitudinal section, illustrating a pile structure stabilized in an earth formation by a solidified mass and further showing the general arrangement of a preferred apparatus in accordance with the invention;

FIGURE 2 is a vertical section through the bottom of a hollow pile illustrating a preferred embodiment of the hole configuration therein;

FIGURE 3 is a transverse sectional view illustrating a variation in the size and shape of the solidified mass;

FIGURE 4 is a vertical section through the lower end of a modified pile structure stabilized in an earth formation by a solidified liquid mix in accordance with the invention; and

FIGURE 5 is a schematic elevation, partially in longitudinal section, of another aspect of the invention.

Referring to FIGURE 1 of the drawing, a reservoir 10 containing a liquid 11 is shown resting on the surface 12 of the earth. A hollow conduit 13 leads from inside reservoir 10 to a pump 14. Similarly, the conduit 15 having a pressure gauge 16 and a flexible coupling 17 connects the pump 14 to the top of a hollow cylindrical closed-bottom pile structure shown generally at 18. The pile 18 is shown penetrating into a generally unconsolidated earth formation 19 of loose materials such as sand and/or gravel and has a removable top closure 21. A neoprene ball 22 has a diameter approximately equal to the internal diameter of the pile 18 as shown positioned near the lower end of the pile where it has been pumped in the direction of the arrow. The bottom of the pile is closed by a closure 24 of any suitable configuration. Near the closed bottom 24 of the pile 18 a series of holes 25 are provided so that a resin-forming composition 26 may flow from within the pile out into the surrounding earth formation 19. An internal annular shoulder member 23 prevents passage of the ball 22 into the lowermost portion of the pile 18 thereby preventing the reservoir liquid 11 from passing out into the formation.

As shown in FIGURE 2, a preferred form of hole configuration near the bottom 24 of the pile 18 comprises three layers of four holes wherein the four holes of each layer are spaced 90° apart. Each layer is rotated 45° with respect to the adjacent layer(s) and there is provided a three-inch spacing between the layers to insure a uniform flow of the liquid composition 26. The provision of this type of hole configuration causes the liquid material 26 to form a solid mass or plug-like collar completely surrounding the lower end of the pile 18 (See FIGURE 1). It is sometimes desirable to cause the material 26 to form button-like projections on the external surface of the pile 18. Such a result can be achieved through suitable spacing of the holes 25 or by forcing a lesser amount of liquid material 26 out into the formation 19. Thus, in FIGURE 3 there is shown a cross section of a pile which has been stabilized in an unconsolidated earth formation 19 by solidified projections 27 of our liquid material.

FIGURE 4 illustrates a hollow pile 20 having a lower end of slightly modified construction from that shown in FIGURES 1-3. As shown, the lower end of the modified pile is provided with a reduced-diameter portion 29 having radially projecting struts or members 30. The struts or members 30 may take the form of annular disc or they may be rod-shaped. In either case, they are positioned in longitudinally spaced relation along the reduced-diameter portion 29 so as to alternate with the layers of holes 25.

The use of struts 30 forms a series of ledges which materially increases the shear resistance of the solidified resin collar 31 to pull-out forces, especially in relatively hard or compact earth formations as shown at 32.

In accordance with the present invention the hollow, closed-bottom pile 18 of FIGURE 1 is first driven into the earth formation 19 to the desired depth. To prevent the infiltration of sand and other loose materials into the bottom of the pile 18, during driving, the holes 25 are closed by means of cores, metal chisel plugs, or a suitable metal adhering tape. After the pile has been driven the desired amount of a solidifiable liquid resin composition, e.g., prepared according to the example, is poured into the pile. The neoprene ball 22, used as a separator, is then inserted into the top of the hollow pile; and the top is thereafter closed by connecting the closure 21 and the flexible coupling 17 thereto. Operation of the pump 14 displaces the neoprene ball 22 downwardly toward the closed bottom 24 of the pile by pumping water 16 into the reservoir 10. This operation breaks the plugs from the holes 25 and thereby causes the liquid mix 26 to flow out through said holes 25 and into the surrounding earth formation 19 as shown in FIGURE 1. Initially the liquid mix tends to creep along and surround the external walls of the pile displacing water therefrom after which the projecting portions of the mix mingle with the surrounding earth to reinforce the pile and strengthen the same as will be readily understood. The earthy material adjacent the body of the pile becomes impregnated with the liquid mix, which when it sets or hardens not only reinforces the pile itself but reinforces and hardens the surrounding earthy material and this greatly increases the pull-out resistance of the pile. When the neoprene ball 22 contacts the annular shoulder 23 located near the bottom 24 of the pile 18, a buildup in pressure or "pressure kick" is noted on the gauge 16; the pump is then ceased, and the liquid mix 26 is allowed to solidify.

It is to be understood that other suitable methods and apparatus for forcing the liquid mix out into the formation may be used. Thus, for example, a mechanical plunging may be forced down the hollow pile to displace the liquid mix into the formation. It is also desirable to remove any soil scale from the exterior of the pile near the bottom 24, such as by sand blasting or similar cleaning operations, in order to increase the bond strength of the liquid mix to the metal pile. In addition, the liquid mix
may be forced from within the pile out into the formation in separate components, e.g., by first displacing the curing agent out into the formation and then displacing the polyepoxide or vice versa. Further, the liquid mix may be used to displace and intermingle with the soil and form a solidified enlargement or cluster at any point or at several points throughout the length of the pile structure.

Another and similar application of the liquid mix of our invention relates to the anchoring of guy wires, tension cables, etc. FIGURE 5 schematically shows how the pull-out capacity of a guy line can be increased by forming a bulbous mass of our liquid mix on the lower end of a guy line. In FIGURE 5, 34 represents a hole which has been drilled to the proper depth and angle in an earth formation 35 for receiving a guy line 36. On the lower end of the guy line 36 an irregular shaped member 37 (preferably constructed of metal) is attached to insure a good connection between the guy line 36 and bulb 38 to be formed thereabout. A conduit 39 surrounds the guy line 36 and extends from the surface to a location near the bottom of the hole 34 as shown. The liquid of our invention can be pumped in any suitable manner through the conduit 39 to the desired downhole location. An annular inflatable packer 40 is mounted on the lower end of conduit 39 for sealing off the lower end of the hole 34 so that it can be put under pressure via the conduit 39. It is to be noted that the guy line 36 need not extend upwardly through the conduit 39 but could run alongside the conduit.

In actual practice of this aspect of the invention, the guy line 36 is positioned in the hole 34 and the conduit 39, with the packer 40 attached thereto, is lowered about the guy line 36 to the desired downhole position. The packer 40 is then inflated so as to seal-off the lower end of the hole so that it can be subjected to the pressure applied through conduit 39. The liquid mix of our invention is then pumped down the conduit 39, which provides for positive placement of the liquid mix about the irregular member 37 attached to the lower end of the guy line 36. Continued pumping of the liquid mix forces the latter laterally into the earth formation 35 beyond the extent of the bore 34 where it tends to form a bulbous mass 36 which will set or harden to reinforce the earth formation 35 and increase the pull-out resistance as previously discussed with reference to FIGURES 1 and 4. The packer 40 may be recovered, by deflating it and recovering it and the conduit 39 before the mix solidifies completely. Finally, the hole 34 is back-filled with the earth originally excavated leaving the guy line 36 which has been effectively stabilized by the hardened bulb 38.

Where the earth formation 38 is relatively incompetent or "lose" the liquid mix may flow out into the formation and form the bulb 38 without the application of pressure through the conduit 39. In such an instance it is unnecessary to use the sealing packer 40.

We claim as our invention:

1. A method of installing a generally cylindrical, hollow, closed-bottom pile member having perforations in a section of the wall near the bottom end thereof in an earth formation comprising:
   - driving said pile member into an earth formation, said earth formation tightly engaging the outer surface of said pile member at least along the perforated section thereof when said driving is completed;
   - disposing said perforated section of said pile member within an unconsolidated portion of said earth formation;
   - displacing through said pile member and said perforations a liquid thermo-setting resin-forming composition;
   - permeating said unconsolidated portion of said formation with said liquid composition in a radially extensive zone that is continuous from within the piling out into said unconsolidated portion; and
   - solidifying said liquid composition in said radially extensive zone to form a consolidated mass integrally comprising said permeated zone and said pile member.

2. A method as in claim 1 wherein said composition is displaced into the formation by:
   - placing the desired amount of said composition into said pile member;
   - inserting into said pile member a separator means having a diameter substantially equal to the internal diameter of said pile member;
   - applying fluid pressure to said separator means downwardly and thereby displacing said composition through said perforations in the bottom of said pile.

3. A method as in claim 1 wherein a liquid thermo-setting resin-forming composition is a pumppable liquid mixture comprising a polyepoxide and an epoxy resin curing agent.

4. A method as in claim 1 wherein said liquid thermo-setting resin-forming composition is a pumppable liquid mixture of polyepoxide and a stoichiometric excess of a curing agent which possesses a plurality of amino hydrogen atoms.

5. A method of stabilizing a structure embedded in an earth formation comprising:
   - disposing, between at least an external portion of the structure and the surrounding earth, a pumppable liquid mixture of polyepoxide comprising more than one vic-epoxy group and from 5% to 50% stoichiometric excess of a polyamide of a polycarboxylic acid containing at least 7 carbon atoms and an aliphatic polyamine, said polyamine having groups reactive to epoxy groups, said pumppable liquid mixture also comprising a stoichiometric excess of a curing agent which possesses a plurality of amino hydrogen atoms; and
   - solidifying said mixture in intimate and static contact with both the structure and the formation.

6. A method as in claim 5 wherein said curing agent comprises an alcohol-soluble toluene-insoluble aliphatic polyamine containing no more than 30 carbon atoms.

7. A method as in claim 5 wherein the curing agent is 1,3-bis(aminooethylamino)2-propanol.

8. A method as in claim 5 wherein the curing agent is N-(hydroxymethyl)di ethylene triamine.

9. A method as in claim 5 wherein the curing agent is N-(3-sulfolanyl)di ethylene triamine.

10. A method as in claim 5 wherein said liquid mixture comprises a polyepoxide containing only carbon, hydrogen and oxygen and having more than one vic-epoxy group and from 5% to 50% stoichiometric excess of a polyamides of a polycarboxylic acid containing at least 7 carbon atoms and an aliphatic polyamine, said polyamide possessing hydrogen attached to amino nitrogen, and said polyamide having greater affinity to a metal surface than to water and functioning so as to replace water from a metal surface and cure the polyepoxide.

11. A method as in claim 10 wherein the polyepoxide is a glycidyl polyether of a polyhydricphenol having an epoxy equivalency of more than 1.0 and a molecular weight between 250 and 900.

12. A method as in claim 10 wherein the polyepoxide is a reaction product of a polymerized unsaturated fatty acid and an aliphatic polyamine.

13. A method as in claim 10 wherein the polyepoxide is employed in a stoichiometric excess of 5% to 25%.

14. A method as in claim 5 wherein said liquid mixture comprises a glycidyl polyether of a polyhydricphenol having an epoxy equivalency greater than 1.0 and from 5% to 50% stoichiometric excess of a polyamide of a polymerized unsaturated fatty acid and an aliphatic polyamine, said polyamide containing unreacted groups selected from the group consisting of amine and carboxyl groups.

15. A method as in claim 14 wherein the polyamide is a reaction product of a polymerized linoleic acid and di-ethylene triamine.
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16. A method as in claim 14 wherein the glycidyl polyether is a glycidyl polyether of 2,2-bis(4-hydroxyphenol) propane.

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