METHOD OF PREVENTING SCOUR AROUND UNDERWATER STRUCTURES

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FIG. 1
This invention relates to a method of preventing scour or "wash-out" at the mud line of a structure embedded on the bottom of a body of water. The invention has particular application with respect to the prevention of ocean scour around the underwater pile structures used to support offshore drilling and production platforms.

During the past several years considerable interest has been shown in drilling oil wells at offshore locations, particularly in the Continental Shelf off the shores of Texas and Louisiana. The drilling and maintaining of offshore oil wells is a difficult and expensive operation necessitating the use of suitable operation platforms for positioning the required drilling, production and servicing equipment at a safe level above the surface of the waters in which the various operations are being carried out.

Typically, the aforementioned platforms are supported by a plurality of long-legged structures or piles which are driven deeply (200-300 feet) into the ocean floor. Generally, there is sufficient skin friction between the soil and piles of this length to support the platform.

There exists the very real problem, however, of the ocean scouring the bottom soil at the mud line from around the submerged pile structures due to the action of waves, tides and strong underwater currents. This scouring action, in time, often results in a reduction in the skin friction between the mud and the piles so that the piles and platform supported thereon sink deeper into the mud. This settling action can cause considerable dislocation of the drilling and/or production operations and in some instances necessitates a storage of drilling and/or production operations.

The primary object of the present invention is to provide a method of preventing or minimizing the removal of material such as mud and/or unconsolidated sand from about submerged pile structures due to the scouring action of underwater currents and waves.

Broadly, the method of the present invention comprises embedding a pile-like structure in the ocean floor, flowing a liquid resin capable of solidifying underwater into a radially extensive layer that surrounds and contacts the structure at the mud line, and solidifying the resin in intimate and static contact with both the structure and the soil present at the mud line.

Although the scope of the invention is intended to cover resinous substances such as bitumen or asphalt, etc., it is more particularly directed toward certain resin-forming polyepoxide compositions. The preferred resin-forming polyepoxide compositions, which will be described in greater detail infra, are not affected by water, i.e., they will not hydrate or dilute as will concrete or cement. Whereas strong water currents along the ocean floor will excessively dilute and wash away compositions such as cement before it sets, the resin-forming polyepoxide compositions of the present invention are stable against displacement by water currents because they resist dilution in water and possess a very high bonding affinity for most all known substances.

Additionally, the preferred resin mixes will readily adhere to wet surfaces and solidity to form a much stronger bond to metal pileings and earth formations than previously known materials such as cement, etc. Finally, when such a bond-forming resin formulation hardens in place on the ocean floor, it forms an additional layer through which the pile structure penetrates and thereby increases the rigidity of the embedded portion of the structure.

In general a liquid mix suitable for use in the invention basically comprises any resin-forming material capable of solidifying after injection underwater. 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

![Chemical Structure](image)

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 linolate, butyl linolate, ethyl 9,12-octadecadienoate, butyl 9,12,15-octadecatrienoate, butyl elenoate, 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 polyarboxylic 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 polyarboxylic acids, such as, for example, di-(2,3-epoxybutyl)-adipate, di-(2,3-epoxybutyl)-azelate, di-(2,3-epoxyhexyl)-succinate, di-(3,4-epoxybutyl)-maleate, di-(2,3-epoxyoctyl)-pinolate, di-(2,3-epoxybutyl)-phthalate, di-(2,3-epoxyoctyl)-tetraphthalate, di-(4,5-epoxydodecyl)-maleate, di-(2,3-epoxybutyl)-terephthalate, di-(2,3-epoxyphenyl)-thiodipropionate, di-(5,6-epoxytetradecyl)-diarylacboxylate, di-(3,4-epoxybutyl)-sulfanylidibutyrate, tri-(2,3-epoxybutyl) 1,2,4-buttriacboxylate, di-(5,6-epoxypentadecyl)-tartrate, di-(4,5-epoxytetradecyl)-maleate, di-(2,3-epoxybutyl)-azelate, di-(3,4-epoxybutyl)-citrate, di-(5,6-epoxyoctyl)-cylohexane-1,3-carboxylate, di-(4,5-epoxyttetradecyl) 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-epoxyoctyl butyl 3,4-epoxydecylohexanoate; 3,4-epoxy-
3 cyclohexyl 4,5 - epoxyoctanoate; 2,3 - epoxycyclohexyl methyl epoxy cyclohexane carboxylate.

Still another group of the epoxy-containing materials include epoxidized derivatives of polyethylenically unsaturated polyacrylic acids such as, for example, di-methyl 8,9,12,13-di-epoxydecane dicarboxylic acid; dibutyl 7,8,11,12-di-epoxyoctadecane dicarboxylic acid; dioctyl 10,11-diethyl-8,9,12,13-di-epoxy-eicosane dicarboxylic acid; dibenzyl 6,7,10,11 - diepoxyhexa- decane dicarboxylic acid; didecyl 9 - epoxy-ethyl-10,11-epoxyoctadecane dicarboxylic acid; dibutyl 3-buty1-3,4,5,6-epoxyoctylocyclohexane-1,2-dicarboxylate; dicyclohexyl 3,4,5,6-epoxyoctylocyclohexane-1,2-dicarboxylate; dibenzyl 1,2,4,5-epoxyoctylocyclohexane-1,2-dicarboxylate and diethyl 5,6,10,11-diepoxyoctadecane succinate.

Still another group comprises 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-eicosanedioc acid with ethylene glycol, the polyester obtained by reacting diethylene glycol with 2-cyclohexene-1,4-dicarboxylic acid and the like, and made thereto.

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

Another epoxidized group comprises the epoxidized polyesters and copolymers of diolefins, such as butadiene. Examples of this include, among others, butadiene-acrylonitrile co-polymer (Hyca rubbers), butadiene-styrene copolymer and the like.

The epoxide groups 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 epoxide polymers 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 1,1,3,5-tetrakis(4-hydroxyphenyl)pentane (epoxy value 0.514 eq./100 g.) and the like and mixtures thereof.

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

Preparation of polymer 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 such that the temperature is maintained at about 95-97°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 80°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 kettle 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 (percent w.) 0.24, viscosity 70 poises.

Other examples of the glycidyl ethers include the glycidyl ethers of Novolac resins which 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 "methyleny" resins. See Chemical Week, vol. 69, page 27, for September 8, 1951.

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

Curing agents

The curing agents to be combined with the above-described polypeoxides 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 polypeoxides are those which possess a plurality of 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 hydrogens.

Examples of these materials include, among others, the aliphatic polypeoxides, such as, for example, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylen pentamaine, 1,4-diaminobutane, 1,3-diaminobutane, hexamethylene diamine, 3 -(n-isopropylamino)proplamine, N,N',N'- diethyl-1,3-propylene diamine, penta(1 - methylenepropyl)hexamine, tetra- butylenepentamine, hexa-(1,1 - dimethylethylene)heptamine, dia (1-methylbutyl) triamine, pentaamylhexamine, tri(1,2,trimethylethylene)tetramine, tetra(1,3-dimethylylpropylene)pentamine, penta(1,5-dimethylandene)hexamine, penta(1,2-dimethylyl-1-isopropylthylene)hexamine and N,N'- dibutyl-1,6-hexanediamine.

Aliphatic polypeoxides coming under special consideration are the alkyline polyeoxines of the formula

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

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

Preferred aliphatic polypeoxides comprise the polyethylenepolypeoxines of the formula

\[ \text{H}_2\text{N}-\left(\text{CH}_2\text{CH}_2\text{H}_n\right)-\text{H} \]

wherein n is an integer varying from about 2 to 8. Coming under special consideration are the polypeoxines polyamines comprising 20-80% by weight of polypeoxine polyamines having average molecular weights in the range of 200-500. These high molecular weight polypeoxine polyamines normally start with tetraethylene pentamine and having related higher polyamines 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, percent 8

Viscosity, poises 75-250

Equivalent weight, percent 42.5 to 47.5

Other examples include the polipeoxines possessing a cycloaliphatic ring or rings, such as, for example, 1-cyclohexylamine - 3 -aminopropane, 1,4 - diaminoocyclohexane, 1,3 - diaminocyclopentane, di(aminocyclohexyl)methane, di(aminocyclohexyl)sulfone, 1,3 - di(amin-
cyclohexyl)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 alkylo-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 amine. Thus, di(aminocyclohexyl) methane is obtained by hydrogenating methylene diamine.

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 group or substituted amino group or groups are attached to carbon, such as in the alkoxyxylpropamines as triethoxyxylpropamines.

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

Still another group comprise the polymeric polyamines, such as may be obtained by polymerizing or copolymerizing unsubstituted amine groups, such as allyl amine or dialkyl 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 methylacrolein 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 propyleneoxide-1 and methyl acrylate, and then reacting this with a polyamine so as to effect an exchange of the 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-(aminomethyl) piperazines, such as, for example, N-aminoethylpiperazine, N - aminoisopropyl - 3 - butoxypiperazine, N-aminomethylpiperazine, 2,5 - dibutyl - N - aminomethylpiperazine, 2,5-dieutyl-N-aminomethylpiperazine and the like. Coming under special consideration are the N-(aminomethyl) piperazines wherein in the alkyl group in the aminomethyl 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 monopoxide. Examples of these reactants include, among others, ethylene oxide, propylene oxide, styrene oxide, phenyl glycidyl ether, allyl glycidyl ether, octadecyl glycidyl ether, toly glycidyl ether, chloroethyl glycidyl ether, naphthyl glycidyl ether, diacetate of monomethyly ether of glycerol, propionate of the monoglycidyl ether of glycerol, epichlorohydrin, 1,2-decylene oxide, glycidyl acetate, glycidyl benzote, glycidyl propionate, glycidyl acrylate, glycidyl methacrylate, glycidyl stearate, glycidyl oleate, butyl 1,2-epoxypropylpropionate and the like.

This reaction between the polyamines and monopoxide 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 mole of monopoxide. The excess amine can be retained or removed by distillation. Examples of the monoepoxide-polyamine reaction products include, among others, N-(hydroxypropyl) diethylenetriamine (reaction product of propylene oxide and diethylenetriamine) and N-(2-hydroxy-4-phenyloxopropyly) diethylenetriamine (reaction product of phenyl glycidyl ether and diethylenetriamine).

A group of related materials are those soluble fusible products obtained by reacting a polyoxide with a monoa mine. Examples of polyoxides that may be used include any of those noted above for use in the compositions of the present invention. Examples of the monoa mines include, among others, secondary amines as diethylenetriamine, diethylenetriamine, dipropylamine, dibutyl amine, di(tertbutyl)amine, dimethyamine, dicyclohexyl amine, diallylamine, dibenzylamine, methylaminamine, ethylicoxylpropylamine and the like. This reaction between the polyoxides and monoa mines is effected by merely bringing the components together in proper proportions. The desired fusible fusible products are obtained when the polyoxide and monoa mine are combined so as to have at least 1.5 mols of the amine per epoxide equivalent of the polyoxide.

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

wherein x represents an integer in the range of 0 through 3 and A and A' represent 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 nontertiary 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 heteroaromatic 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 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 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-ketomyristic acid, 8,10-dibromostearic acid, margaric acid, stearic acid, alpha-chlorostearic acid, linoleic acid, oleic acid, dihydroxystearic acid, arachidic acid, elapanodonic acid, behenic acid, lignoceric acid, cerotic acid, montanolic acid, melissic acid, and the like, and mixtures thereof. These imidazoline 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 equvalent 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-ethylythio-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-butythio-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-(alkylthiohydroxylalkyl) aliphatic and aromatic polyamines, the N- (cycloalkylthiohydroxyalkyl) aliphatic and aromatic polyamines and the N-acylthiohydroxyalkyl aliphatic and aromatic polyamines. Preferred phosphorus-containing curing agents include the N- (dialkylphosphinothiohydroxylalkyl) aliphatic and aromatic polyamines, the N- (dicycloalkylphosphinothiohydroxylalkyl) aliphatic and aromatic polyamines, and the N- (diaminophosphinothiohydroxylalkyl) 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

\[
NHR-\left(\begin{array}{c}
\vdots \\
H \end{array}\right)\text{NH}
\]

wherein \(x\) is an integer of 0 to 10 and R is a bivalent hydrocarbon radical containing from 1 to 10 carbon atoms, and derivatives obtained by reacting the aforesaid polyamines with monooepoxides 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 —OH groups, sulfolanyl groups and the like. Examples include, among others, N-(2,3-dihydroxypropyl) diethylene triamine, N-(hydroxyethyl) diethylene triamine, N-(2-hydroxy-3-allyloxypropyl) diethylene triamine, N-(hydroxyethyl) ethylene diamine, N-(hydroxyethyl) triethylene tetramine and the like, N-(3-sulfolanyl) diethylenetriamine, N-(3-sulfolanyl) ethylenetriamine, N- (3-sulfolanyl) ethylene diamine, N-(2,3-dihydroxypropyl) diethylene triamine, N-(hydroxyethyl) ethylene diamine, N-(hydroxyethyl) triethylene tetramine and the like, N-(3-sulfolanyl) diethylenetriamine, N-(3-sulfolanyl) ethylenetriamine, N-(3-sulfolanyl) ethylene diamine. Other examples of the hydrogen-containing polyamines can be found in the patent to Newey—U.S. 2,864,775, and examples of the sulfolanyl-substituted polyamines 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 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-decandioic acid, 1,2-dodecanedioic acid, 1,20-eicosadenedioic acid, 1,14-tetradecanedioic acid, 1,18-octadecanedioic 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 lower aliphatic esters of drying oil esters so as to prevent decarboxylation 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 59 (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, oleic acid, and linumic acid, such as may be derived from oils, such as soybean oil, linseed oil, olive oil, perilla, olibica, 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 residual monomer. The aliphatic polyamides used in preparing the polyamides may be any di- or 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-isopropylamino)propylamine, and the like. Particularly preferred polyamides are those containing from 2 to 12 carbon atoms, and especially those of the formula

\[
\text{HN-NR-NR-NH}
\]

wherein \(x\) is an integer of 0 to 10 and R is a bivalent hydrocarbon radical containing from 1 to 10 carbon atoms. Coming under special consideration are those polyamides 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 polyamides containing now 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 numbers between 50 and 450. Amino 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 fluid polyamides produced by the condensation of polymerized linoleic 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 attached to amino nitrogen atoms or carboxyl hydrogen atoms. Such products are obtained by controlling the proportion of reagents so that there is always at least one amino hydrogen or carbonyl group, such as, for example, by using an excess of the polyamine reactant. A process for making such polyamides (10
obtain free amino groups) or an excess of acid (to obtain carboxyl groups) is illustrated in U.S. 2,450,940 and U.S. 2,695,908 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 depending chiefly on their reactivity with these materials. Among the preferred accelerators are phenolic compounds, tertiary amines, mercaptans and those 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 amino curing agent.

The proportions of the polyepoxide and the material having the amino hydrogen that is 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 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 alicyclic, 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, alkane 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, as 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° 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., an 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 aromatic solvent with admixture of hydrocarbon containing a greater proportion of non-aromatics, e.g., unextracted kerosenes, gas oils or the like. an general, oil boiling above 175°, and preferably between 350° and 650° 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. Preferably, 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.

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 the dimerized 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>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamide of dimerized linoleic acid and diethylene amine having an amine value of 306</td>
<td>80</td>
</tr>
<tr>
<td>Polyether A</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 of an offshore platform provided with pile structures which have resin scour plates formed in situ thereabout;

**FIGURE 2** is an enlarged schematic elevation, partially in section, illustrating the effect of ocean scour on the mud line surrounding an unprotected pile;

**FIGURE 3** is an enlarged schematic elevation, partially in section, of a pile structure having a resin scour plate formed thereabout in accordance with the present invention;

**FIGURE 4** is an isometric view of a pile structure provided with a resin scour plate in accordance with the invention;

**FIGURE 5** is a schematic elevation showing the general arrangement of a preferred form of apparatus to be used in practicing the method of the present invention; and,

**FIGURE 6** is a schematic elevation, partially in longitudinal section, of a modified embodiment of apparatus to be used in accordance with the method of the present invention.

Referring to **FIGURE 1** of the drawing there is illustrated a substructure 10 which supports a platform 11 and a suitable drilling tower 12 at a safe distance above the surface of a body of water. It is to be understood that the platform 11 might also support certain production equipment such as a Christmas tree, etc.

The substructure 10 comprises a minimum of three legs or pile structures 13 and preferably four such piles are used. The piles 13 which are generally formed of metal are rigidly held together by structural bracing 14. The piles 13 may be from 200 to 300 feet in length so as to support the substructure 10 and the platform 11 mounted thereupon. The weight of the substructure 10 and the platform 11 is supported mainly by the skin friction between the mud and the outer surface of the piles 13 over their entire embedded length.

At the mud line the piles 13 are provided with resin scour plates 15 formed in situ in accordance with the present invention to prevent the action of ocean water currents, tides and waves from scouring away the mud and loose soil from around the piles.

**FIGURE 2** illustrates the manner in which the water scouring action at the mud line carries away the bottom soil from around the outer surface of a pile 13. As shown, this scouring action can result in a reduction in the skin friction effect between the mud and the outer surface of the pile 13 (as denoted at X in **FIGURE 2** so that the piles and platform supported thereon sink deeper into the mud. As a result of such "pile sinking" action, drilling and/or production operations may be completely disrupted and in some instances it is entirely possible that entire platforms might collapse.
As best shown in FIGURES 3 and 4, the problem of the ocean scouring away the soil from about the piles 13 at the mud line may be eliminated by forming a resin scour plate or plate by extending outwardly in all directions from the pile 13. Preferably a preferred mix of resin-forming material as set out supra is used to form the scour plate 15.

Such a preferred mix tends to flow down into and intermingle with the soil at the mud line (see FIGURE 3) forming a bonded mass 16 which will effectively prevent ocean scour caused by water currents, etc., from carrying away the soil from about the pile 13. Additionally, the preferred resin forming mixes used in the method of the present invention have a high bonding affinity for metal so that after the resin scour plate 15 has been emplaced on the ocean floor it acts as an additional layer of cross bracing increasing the rigidity of the embedded portion of the pile structure 12.

FIGURE 5 illustrates a preferred embodiment of apparatus for carrying out the method of the present invention. The method comprises: (a) forming a plurality of openings 23 evenly spaced about its bottom circumference so that the liquid resin will be uniformly placed in a zone extending radially outwardly from the pile 17 as shown by the arrows 24. Thus, a continued controlled pumping will cause the liquid resin composition to flow down pipe 26, out through openings 23 and creep outwardly in all directions from about the pile 17, intermingling with the soil at the mud line (best shown at 16 in FIGURE 3) and solidifying in situ with both the soil and pile to form a scour plate as shown in FIGURES 1, 3 and 4. FIGURE 6 illustrates an alternative embodiment of apparatus which can be used to practice the method of the present invention in those instances where the metal pile is hollow. As shown, the hollow metal pile 26 has a plurality of holes or slots 27 which may be cut into the pile from the outside thereof by divers after the pile is driven in place. To prevent weakening of the pile 26 caused by the holes 27, perforated plate members 28 are welded in place. A suitable packer 29 is then lowered down through the pile 26 and sealed in place below the apertures 27 to pack-off the lowestmost portion of the pile. Subsequently, pipe 30 is lowered into position as shown, through which the liquid resin may be pumped radially outwardly about the pile in the direction of arrows 31. If desired, the pipe 30 may protrude through another packer (not shown) positioned above the slots 27 to ensure that the pipe 30 is properly positioned and that the liquid is forced outwardly under adequate pressure.

It is to be understood that various other apparatus could be used in practicing the method of the present invention. For example, a dump bailer may be used to convey the solidifiable liquid resin down to the mud line after which a diver or divers could spread the resin into a radial zone surrounding the pile. Also, a mechanical plunger may be forced down a hollow pile to displace the liquid mix out into a radial layer surrounding the pile at the mud line. The radial extent of the zone covered by the resin scour plate varies with degree of natural consolidation of the soil at the mud line and the intensity of the scouring action encountered at any given location. Generally, the scour plate should be many times the diameter of the pile.

I claim as my invention:

1. A method of installing an elongated structural member in an offshore earth formation where the ocean floor comprising the water comprises a mud line which is unconsolidated, said method comprising:
   (a) emplacing a portion of said member within the earth formation;
   (b) displacing a layer of solidifiable liquid resin-forming composition out into a radial zone surrounding said member at the mud line; and,
   (c) solidifying said liquid composition in intimate and static contact with both said member and the ocean floor at the mud line.

2. A method as in claim 1 wherein said radial zone is approximately 10 times the diameter of said structural member.

3. A method of forming a permanent resin scour plate about a structure embedded in an offshore earth formation having unconsolidated soil at the mud line, said method comprising:
   (a) driving the structure into the earth formation;
   (b) providing means for flowing a liquid resin-forming composition from a surface location to a portion of said structure located near said mud line;
   (c) flowing said liquid resin-forming composition radially outwardly to form a layer; and,
   (d) solidifying said layer in intimate and static contact with both the portion of said structure located near the mud line and the soil present at said mud line.

4. A method as in claim 3 wherein:
   (a) said structure is hollow; and,
   (b) said solidifiable resin-forming composition is disposed down through said structure and outwardly, through holes formed in said structure near the mud line, into a radially extending layer.

5. A method of forming a permanent scour plate about a structure embedded in an offshore earth formation having unconsolidated soil at the mud line, said method comprising:
   (a) driving the structure into the earth formation;
   (b) disposing radially outwardly from the structure at the mud line a layer of a pumpable liquid mixture comprising a polyepoxy and an epoxy resin curing agent; and,
   (c) solidifying the mixture in intimate and static contact with both said structure and the soil present at the mud line.

6. A method of forming a permanent scour plate about a structure embedded in an offshore earth formation having unconsolidated soil at the mud line, said method comprising:
   (a) driving the structure into the earth formation;
   (b) disposing radially outwardly from the structure at the mud line a layer of a pumpable liquid mixture of polyepoxide and a stoichiometric excess of a curing agent which possesses a plurality of amino hydrogen atoms; and,
   (c) solidifying the mixture in intimate and static contact with both said structure and the soil present at the mud line.

7. A method as in claim 6 wherein said liquid mixture comprises a polyepoxide having 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 polypeptide having groups reactive with epoxy groups.

8. A method as in claim 6 wherein said curing agent comprise an alcohol-soluble toluene-insoluble aliphatic polyamine containing no more than 30 carbon atoms.
9. A method as in claim 6 wherein the curing agent is 1,3-bis(aminooethylamino)2-propanol.

10. A method as in claim 6 wherein the curing agent is N-(hydroxyethyl)diethylene triamine.

11. A method as in claim 6 wherein the curing agent is N-(3-sulfonanyldiethylene triamine.

12. A method as in claim 6 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 polyamide 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 displace water from a metal surface and cure the polyepoxide.

13. A method as in claim 12 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.

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

15. A method as in claim 12 wherein the polyamide is employed in a stoichiometric excess of 5% to 25%.

16. A method as in claim 6 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.

17. A method as in claim 16 wherein the polyamide is a reaction product of a polymerized linoleic acid and diethylene triamine.

18. A method as in claim 16 wherein the glycidyl polyether is a glycidyl polyether of 2,2-bis(4-hydroxyphenol) propane.

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