



Description

The present invention relates to a novel process for lining the inner surfaces of pipes or pipe sections by the so-called Insituform method using certain binders (mixtures of resin and curing agent) and to the products produced thereby.

It is known to use the Insituform method for lining or repairing pipes or pipe sections, in particular man-sized or narrower underground pipes and mains, such as sewers, gas and water mains or oil pipelines. This method comprises using a feed or inversion pipe to introduce into the mains which is to be lined or restored a tubular flexible laminate made up of an essentially liquid-impermeable membrane made of, for example, polyvinyl chloride, polyethylene, polyester or polyurethane, and a fibrous layer which has been impregnated with a binder which is not as yet fully cured. As the tube is introduced the layer of the tube which is impregnated with the binder or resin faces towards the centre of the tube at first. After one end of the tube has been attached to the end of the pipe which is to be lined, water is pumped under pressure into the inversion pipe, and the tube inverts and is pressed with the side impregnated with the resin against the inner surface of the pipe. The resin is generally cured to completion by pumping hot water into the inversion pipe.

Hitherto the resins used with this method have been

31

in the main unsaturated polyester resins. These polyester resins have the disadvantage that on curing they undergo relatively marked shrinkage and have insufficient bond strength to the substrate and a limited shelf-life at temperatures above 25°C. Moreover, unsaturated polyesters generally contain considerable proportions of styrene and have to be cured by means of peroxides [cf. for example the Synolite[®] brochure 593-61 0050 from the manufacturing company SYNRES]. Styrene has an unpleasant odour and, inter alia, a low flash point (31-32°C) and a high evaporation number. Furthermore, its high vapour pressure makes it unsafe from the point of view of industrial hygiene.

Unsaturated polyester resins are unsuitable, for example, for relining gas mains, since gas residues, such as tar, impair the curing of the resins. Nor, owing to the unpleasant odour and taste of styrene which cling to them, can they be used for lining water mains. Furthermore, they are advantageously not used for mains in the groundwater belt, since, owing to the poor adhesion of the resin, groundwater can penetrate between the inner surface of the pipe and the lining. The pressure of the groundwater then frequently causes large bubbles in the coating, thereby impeding, inter alia, the free flow of the medium to be transported.

Epoxy resin/curing agent systems have actually been used before in the Insituform process. These systems, in which aromatic or aliphatic polyamines acted as the curing agent, are distinguished from polyester resins by improved adhesive strength, lower shrinkage and superior mechanical properties, such as increased tensile shear strength. However, they leave a great deal to be desired as regards shelf-life, curing temperatures and/or viscosity [cf. for example British Patents 1,340,063 and 1,449,455; Gas-Wasser-Abwasser, 61, 45-48 (1981); and "Polyester for relining underground pipes" in Australian Plastics and Rubber, October 1980].

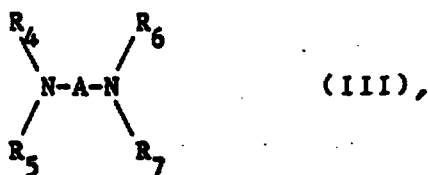
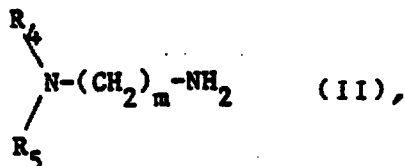
The invention accordingly provides a process for lining the inner surfaces of pipes or pipe sections using the Insituform method by pressing a tubular flexible laminate

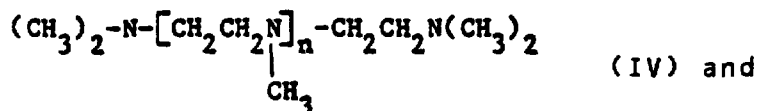
- made up of an essentially liquid-impermeable membrane and a fibrous layer which has been impregnated with a binder (resin mixture) which is not as yet fully cured with the face with the binder against the inner surface of the pipe by means of
- 5 liquid pressure in such a way that the laminate takes on the shape of the inner surface of the pipe and the binder becomes fully cured in this state, forming a firmly adhering internal lining, wherein the laminate used has been impregnated with a binder which contains
- 10 (a) a curing agent which is a salt of one or more (poly)-amines having at least one tertiary nitrogen atom and one or more aromatic polyols or one or more aliphatically substituted phenols, the aliphatic radical having at least 9 carbon atoms, and
- 15 (b) a liquid epoxy resin or a liquid mixture of epoxy resins and can, if desired, also contain
- (c) further additives.

Said salts (a) can be prepared from basically any aliphatic, araliphatic, aromatic or heterocyclic (poly)amine having at least one tertiary nitrogen atom. Amines of this

20 type can also be substituted (on carbon atoms), for example by halogen atoms, such as chlorine or bromine atoms, OH or CN groups, phenyl groups, C₅₋₈-cycloalkyl groups, alkyl or alkoxy groups each having 1-4 carbon atoms or aminoalkyl groups having 1-12 and in particular 1-4 carbon atoms.

25 Examples of suitable amines of at least partly aliphatic character are those of the formulae I-V

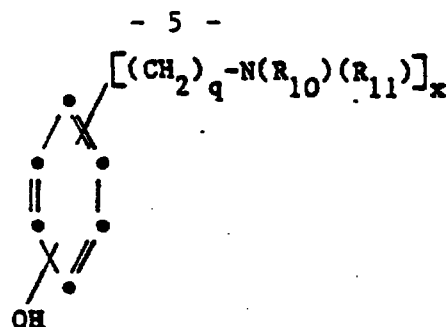




in which m is 2-6, in particular 2 or 3,
n is zero, 1 or 2,

- 5 R_1 is C_{1-12} -alkyl, in particular alkyl having 1-8 and especially 1-4 carbon atoms, hydroxyalkyl having 1-4 carbon atoms or alkoxyalkyl having a total of 2-6 carbon atoms,
 R_2 and R_3 , independently of the other, are each the same as R_1 or are each unsubstituted or substituted phenyl, benzyl, phenylethyl, cyclopentyl or cyclohexyl,
- 10 R_4 is C_{1-4} -alkyl, in particular ethyl and especially methyl,
 R_5 is C_{1-4} -alkyl, in particular ethyl and especially methyl, cyclopentyl or cyclohexyl,
 R_6 is C_{1-12} -alkyl, in particular alkyl having 1-8 and especially 1-4 carbon atoms, phenyl, benzyl, phenylethyl, benzoyl, cyclopentyl, cyclohexyl, $-A_1CN$ or $-A_1CH_2NH_2$,
- 15 R_7 is hydrogen or $-A_1CH_2NH_2$ or
 R_6 and R_7 together are $-(CH_2)_p-$ with $p = 4$ or 5 ,
 $-(CH_2)_2O(CH_2)_2-$ or $-(CH_2)_2NH(CH_2)_2-$,
 R_8 is $-OR_9$, $-O-C(=O)R_9$, $-O-C(=O)NHR_9$, $-O-A_1CN$, $-O-A_1NH_2$, $-O-C(=O)-A_1-N(CH_3)_2$,
20 $-O-C(=O)-Y-C(=O)-A_1-N(CH_3)_2$ or $-O-Y_1-O-A_1-N(CH_3)_2$,
 R_9 is C_{1-12} -alkyl, especially C_{1-4} -alkyl, phenyl, benzyl, cyclopentyl or cyclohexyl,
 A and A_1 , independently of the other, are each ethylene or 1,2- or 1,3-propylene,
- 25 Y is the direct bond, $-C_rH_{2r}-$ with $r = 2-10$, in particular 2-6, phenylene, toluylene or cyclohexylene and
 Y_1 is $-C_rH_{2r}-$ with $r = 2-10$, in particular 2-6, phenylene, toluylene or cyclohexylene.

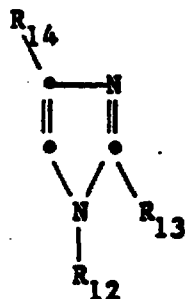
Also suitable are tertiary aminophenols of the formula VI



(VI)

in which q is 1 or 2, x is 1, 2 or 3, and R_{10} and R_{11} , independently of the other, are each C_{1-4} -alkyl, in particular methyl or ethyl. Examples of compounds of the formula VI are dimethylaminomethylphenol, diethylaminomethylphenol, bis(dimethylaminomethyl)phenols, bis(diethylaminomethyl)phenols, bis(diethylaminoethyl)phenols [sic] and especially 2,4,6-tris(dimethylaminomethyl)phenol.

Heterocyclic tertiary amines can be saturated or unsaturated and can be unsubstituted or substituted, for example by halogen atoms or alkyl, phenyl or benzyl groups. Suitable are for example unsubstituted or substituted pyrazoles and imidazoles and N-substituted pyrroles, pyridines, pyrazines, indoles, piperidines and piperazines. Possible N substituents are in particular alkyl groups having 1-4 carbon atoms or phenyl or benzyl groups. Examples of heterocyclic structures of this type are N-methylpyrrole, pyrazole, N,N'-dimethylpyrazine and N,N'-diethylpyrazine, N-methylindole, N-ethylindole, N-methylpyridine, N-ethylpyridine, N-benzylpyridine, N-methylpiperidine, N-ethylpiperidine, N-isopropylpiperidine, N,N'-dimethylpiperazine and N,N'-diethylpiperazine. The heterocyclic tertiary amines are preferably imidazoles of the formula VII



(VII)

in which R_{12} is hydrogen, C_{1-4} -alkyl, phenyl or benzyl, and R_{13} and R_{14} , independently of the other, are each hydrogen, a halogen atom, such as chlorine or bromine,

C₁₋₄-alkyl, phenyl, cyclohexyl or benzyl. Examples are imidazole, 2-chloroimidazole, 2-methylimidazole, 2-ethylimidazole, 2-n-propylimidazole, 2-phenylimidazole, 4-methylimidazole, 4-n-propylimidazole, 2-methyl-4-phenylimidazole, 2-cyclohexyl-4-methylimidazole and 2-ethyl-4-methylimidazole. Preference is given to imidazoles of the formula VII in which R₁₂ and R₁₄ are each hydrogen and R₁₃ is C₁₋₄-alkyl, in particular methyl, ethyl or n-propyl, or phenyl or in which R₁₂ and R₁₃ are each hydrogen and R₁₄ is hydrogen or C₁₋₄-alkyl, in particular methyl, ethyl or n-propyl.

The imidazoles of the formula VII in which R₁₂ is hydrogen can also be used in the form of adducts with polyglycidyl ethers. This is particularly advantageous in the case of unsubstituted imidazole. This preliminary reaction is preferably carried out with diglycidyl ethers of aromatic polyols, in particular bisphenol A [2,2-bis(4-hydroxyphenyl)propane], hydrogenated bisphenol A [2,2-bis(4-hydroxycyclohexyl)propane] or bisphenol F [bis(4-hydroxyphenyl)methane].

Alkyl groups R₁ to R₆ and R₉ to R₁₄, hydroxyalkyl groups R₁ to R₃ and alkoxyalkyl groups R₁ to R₃ can be straight-chain or branched. Examples are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, n-pentyl, 2-pentyl, n-hexyl, n-heptyl, n-octyl, n-decyl and n-dodecyl, hydroxymethyl, 2-hydroxyethyl, 2-hydroxypropyl and 3-hydroxypropyl; and methoxymethyl, ethoxymethyl, 2-methoxyethyl and 2-isopropoxyethyl, respectively.

-C_rH_{2r}- groups Y or Y₁ can likewise be straight-chain or branched, but are preferably straight-chain and have 2-6 carbon atoms.

Substituted phenyl, benzyl, phenylethyl, cyclopentyl or cyclohexyl groups R₂ or R₃ are in particular substituted by chlorine or bromine atoms or methyl, ethyl, methoxy or ethoxy groups. However, said radicals are preferably unsubstituted. Phenylene, toluylene or cyclohexylene Y or Y₁ are in particular 1,3- or 1,4-phenylene, 1,4-toluylene or 1,4-cyclohexylene. A and A₁ are each preferably ethylene or in particular 1,3-propylene.

In preferred compounds of the formula I, R_1 and R_2 , independently of the other, are each C_{1-4} -alkyl or C_{2-4} -hydroxyalkyl and R_3 is C_{1-4} -alkyl, C_{2-4} -hydroxyalkyl, unsubstituted phenyl, benzyl, cyclopentyl or cyclohexyl. In particularly preferred amines of the formula I, R_1 and R_2 are each C_{1-4} -alkyl and R_3 is unsubstituted phenyl and especially unsubstituted benzyl.

In preferred compounds of the formula II, m is 2 or 3, R_4 is methyl or ethyl, and R_5 is methyl, ethyl or cyclohexyl.

In compounds of the formula III, R_4 and R_5 are both preferably ethyl and in particular methyl. R_7 is preferably hydrogen, and R_6 is preferably methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, cyclopentyl, cyclohexyl, benzoyl, 2-cyanoethyl or 3-aminopropyl. Preference is also given to compounds of the formula III in which R_6 is 2-cyanoethyl or 3-aminopropyl and R_7 is 3-aminopropyl. Particular preference is given to compounds of the formula III in which A is ethylene and especially 1,3-propylene, R_7 is hydrogen, and R_6 is 2-cyanoethyl or 3-aminopropyl. Some examples of compounds of the formula III are *N,N*-dimethyl-*N'*-(2-cyanoethyl)ethylenediamine, *N,N*-dimethyl-*N'*-(3-aminopropyl)ethylenediamine, *N,N*-dimethyl-*N'*,*N'*-di-(3-aminopropyl)ethylenediamine, *N,N*-dimethyl-*N'*-(2-cyanoethyl)-1,3-diaminopropane, *N,N*-dimethyl-*N'*-(3-aminopropyl)-1,3-diaminopropane, *N,N*-dimethyl-*N'*,*N'*-(3-aminopropyl)-1,3-diaminopropane and *N,N*-diethyl-*N'*-(benzoyl)-1,3-diaminopropane.

In compounds of the formula IV n is preferably zero or 1.

In the formula V R_8 is in particular $-OR_9$, $-O\overset{\overset{O}{\parallel}}{C}R_9$,

$-O-\overset{\overset{O}{\parallel}}{C}-Y-\overset{\overset{O}{\parallel}}{C}-O-A_1-N(CH_3)_2$ or $-O-Y_1-O-A_1-N(CH_3)_2$. In these groups, R_9 is preferably alkyl having 1-4 carbon atoms, phenyl or benzyl, Y is a direct bond, $-(CH_2)_r-$ with $r = 2-6$ or 1,3- or 1,4-phenylene, Y_1 is $-(CH_2)_r-$ with $r = 2-6$ or 1,3- or 1,4-phenylene and A_1 is ethylene and in particular

43

1,3-propylene. Examples of compounds of the formula V are β -dimethylaminoethyl β -cyanoethyl ether, γ -dimethylamino-propyl β -cyanopropyl ether, β -dimethylaminoethyl γ -amino-propyl ether, γ -dimethylaminopropyl γ -aminoisobutyl ether,
5 β -dimethylaminoethyl acetate, β -dimethylaminopropyl acetate, β -dimethylaminopropyl 2-isobutyrate, γ -dimethylaminopropyl laurate, β -dimethylaminoethyl benzoate, β -dimethylaminoethyl N-phenylcarbamate, β -dimethylaminoethyl carbonate, β -dimethyl-aminoethyl γ -dimethylaminopropyl ether, 1,4-cyclohexyldi(γ -di-methylaminopropyl) ether, di(γ -dimethylaminopropyl) terephtha-
10 late and di(β -dimethylaminoethyl) adipate.

Amines of the abovementioned type are known or can be prepared by methods which are known per se [cf. for example US Patents 4,201,854 and 4,324,739].

15 Particularly preferred amines are compounds of the formula I in which R_1 and R_2 are each ethyl and in particular methyl and R_3 is unsubstituted phenyl and in particular unsubstituted benzyl, especially benzyldimethylamine; amines of the formula II in which m is 2 or 3 and R_4 and R_5 , inde-
20 pendently of the other, are each methyl or ethyl, in particu- lar those in which m is 3 and R_4 and R_5 are both methyl or ethyl; N,N-dimethyl-N'-(3-aminopropyl)-1,3-diaminopropane, N,N-dimethyl-N'-(2-cyanoethyl)-1,3-diaminopropane and in particular N,N-diethyl-N'-(benzoyl)-1,3-diaminopropane or
25 mixtures thereof; compounds of the formula VI in which q is 1 and R_{10} and R_{11} are both ethyl and in particular methyl, x being as defined above; imidazoles of the formula VII in which R_{12} and R_{14} are each hydrogen and R_{13} is hydrogen or C_{1-4} -alkyl; and adducts of said preferred imidazoles, in
30 particular of unsubstituted imidazole, and diglycidyl ethers of bisphenol F, hydrogenated bisphenol A or bisphenol A.

Examples of suitable aromatic polyols for preparing salts (a) are resorcinol, hydroquinone, bis(4-hydroxyphenyl)-methane (bisphenol F), 2,2-bis(4-hydroxyphenyl)propane (bis-
35 phenol A), 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane (tet-rabromobisphenol A), 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 4,4'-dihydroxybiphenyl, bis(4-hydroxyphenyl) sulfone and

novolacs of formaldehyde or acetaldehyde and phenol, chloro-phenol or alkylphenols having up to 9 carbon atoms in the alkyl, in particular cresol novolacs and phenol novolacs. It is preferable to use salts of phenol novolacs and in particular of resorcinol, bisphenol F or bisphenol A and the above-mentioned preferred amines. Very particular preference is given to salts of resorcinol, bisphenol F or bisphenol A and tris(dimethylaminomethyl)phenol, dimethylaminomethylphenol, 2-n-propylimidazole, N,N-dimethylaminopropylamine, N,N-diethylaminopropylamine or N,N-diethyl-N'-(benzoyl)-1,3-diaminopropane and salts of resorcinol, bisphenol F or bisphenol A and an adduct of imidazole and a diglycidyl ether of bisphenol A or bisphenol F.

Particularly suitable aliphatically substituted phenols are alkylphenols, alkenylphenols, alkadienylphenols and alkatrienylphenols having 9-18 and in particular 9-16 carbon atoms in the alkyl, alkenyl, alkadienyl and alkatrienyl groups. And these aliphatic groups can be straight-chain or branched, but are preferably straight-chain. Examples of aliphatically substituted phenols are 3- and 4-n-nonylphenol, 3-n-decylphenol, 4-n-dodecylphenol, 4-n-tetradecylphenol, 4-n-pentadecylphenol, 4-n-octadecylphenol, 4-(2-nonenyl)phenol, 3-(4-decenyl)phenol, 4-(2-dodecenyl)phenol, 3-(9-octadecenyl)phenol, 4-(1,3-decadienyl)phenol, 3-(9,13-octadecadienyl)phenol, 3-(n-pentadecatrienyl)phenols, such as 3-(2,4,6-pentadecatrienyl)phenol extracted from cashew nuts and known as "Phenol CNSL", and 4-(9,11,15-octadecatrienyl)phenol. Preference is given to 3- and 4-n-nonylphenol and to 3-(2,4,6-pentadecatrienyl)phenol, in particular their salts with 2-n-propylimidazole or tris(dimethylaminomethyl)phenol. However, in general salts (a) are preferably salts of the defined type of (poly)amine and aromatic polyol.

The invention also relates to those of the salts (a) specifically developed for carrying out the process according to the invention which are novel. Particular preference is given to salts of resorcinol and 2-n-propylimidazole, especially to the 2:1 salt of resorcinol and 2-n-propylimidazole.

(45)

Said salts (a) can be prepared in a manner known per se by reacting (poly)amines having at least one tertiary nitrogen atom and aromatic polyols or phenols of the type defined, and generally by raising the reaction temperature to between 80 and 150 and especially 100 and 130°C. The reactants for this reaction are advantageously employed in such amounts that there are 1 to 2 OH equivalents per nitrogen equivalent. Salts (a) are liquid to highly viscous. Their viscosity can be regulated, if desired, with suitable diluents, especially high-boiling organic solvents. Examples of suitable solvents and diluents are benzyl alcohol, furfuryl alcohol, cyclopentanol, cyclohexanol, pine oil and cyclic ketones, such as cyclopentanone and cyclohexanone. The diluents are generally used in amounts of 20-80% by weight, preferably 20-50% by weight, based on salt (a). The preferred diluent is benzyl alcohol.

Instead of salts (a) it is also possible to use in the process according to the invention mixtures of aromatic diols, such as resorcinol and bisphenols, especially bisphenol A or bisphenol F, with salts of compounds of the formula VI and saturated or unsaturated, straight-chain or branched aliphatic monocarboxylic acids. Which of the compounds of the formula VI are preferred is subject to what was stated above. Suitable aliphatic monocarboxylic acids are in particular those having up to 18 carbon atoms and especially saturated or unsaturated aliphatic monocarboxylic acids having 6-18 carbon atoms. Examples of suitable monocarboxylic acids are: acetic acid, propionic acid, butyric acid, isobutyric acid, caproic acid, 2-ethylcaproic acid, capric acid, lauric acid, palmitic acid, stearic acid, oleic acid and the highly branched monocarboxylic acids known as "versatic acids". Preferred salts for these mixtures are dimethylaminomethylphenol 2-ethylhexoate or oleate and in particular tris(dimethylaminomethyl)phenol trisoleate and especially tris(dimethylaminomethyl)phenol tris-2-ethylhexoate. The viscosity of said mixtures can likewise be set if desired to the desired value by adding diluents, in particular those of the

abovementioned type. The salts of compounds of the formula VI and saturated or unsaturated aliphatic monocarboxylic acids are known or can be prepared by methods known per se.

5 Suitable epoxy resins (b) are in particular epoxy resins having on average more than one group which is bonded to a hetero atom, for example to a sulfur and preferably an oxygen or nitrogen atom, and has the formula VIII



10 where Q and Q₂ are both a hydrogen atom and Q₁ is a hydrogen atom or a methyl group or Q and Q₂ together are -CH₂CH₂- or -CH₂CH₂CH₂- and Q₁ is a hydrogen atom.

15 Examples of resins of this type are polyglycidyl and poly(β-methylglycidyl) esters which are derived from aliphatic, cycloaliphatic or aromatic polycarboxylic acids. Examples of suitable polycarboxylic acids are succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dimerised or trimerised linoleic acid, tetrahydrophthalic acid, 4-methyltetrahydrophthalic acid, hexahydrophthalic acid, 4-methylhexahydrophthalic acid, phthalic acid, isophthalic acid
20 and terephthalic acid.

25 Further examples are polyglycidyl and poly(β-methylglycidyl) ethers which are obtained by reacting a compound which contains at least two alcoholic and/or phenolic hydroxyl groups per molecule with epichlorohydrin or with allyl chloride and subsequently epoxidizing with per-acids.

30 Examples of suitable polyols are ethylene glycol, diethylene glycol, poly(oxyethylene) glycols, propane-1,2-diol, poly(oxypropylene) glycols, propane-1,3-diol, butane-1,4-diol, poly(oxytetramethylene) glycols, pentane-1,5-diol, hexane-2,4,6-triol, glycerol, 1,1,1-trimethylolpropane, pentaerythritol, sorbitol, resorcinol, quinitol, bis(4-hydroxycyclohexyl)methane, 2,2-bis(4-hydroxycyclohexyl)propane, 1,1-bis(hydroxymethyl)cyclohex-3-ene and also aromatic

47

polyols of the type mentioned above in the preparation of salts (a).

Suitable poly(N-glycidyl) compounds are obtained by dehydrochlorinating products of reacting epichlorohydrin with amines having at least two amine-hydrogen atoms. Examples of suitable amines are aniline, n-butylamine, bis(4-aminophenyl)methane, 1,3- and 1,4-xylylenediamine, 1,3- and 1,4-bis(aminomethyl)cyclohexane and bis(4-methylaminophenyl)-methane. Further suitable compounds of this type are tri-glycidyl isocyanurate, N,N'-diglycidyl derivatives of cyclic alkyleneureas, such as ethyleneurea and 1,3-propyleneurea, and hydantoins, such as 5,5-dimethylhydantoin.

Examples of poly(S-glycidyl) compounds are the di-S-glycidyl derivatives of dithiols, such as ethanol-1,2-dithiol and bis(4-mercaptomethylphenyl) ether.

Examples of epoxy resins having one or more groups of the formula VIII in which Q and Q₂ together are a -CH₂CH₂- or -CH₂CH₂CH₂- group are bis(2,3-epoxycyclopentyl) ether, 2,3-epoxycyclopentyl glycidyl ether, 1,2-bis(2,3-epoxycyclopentyloxy)ethane, 3,4-epoxy-6-methylcyclohexyl-methyl 3',4'-epoxy-6'-methylcyclohexanecarboxylate and 2-(3,4-epoxy)cyclohexyl-5,5-spiro(3',4'-epoxy)cyclohexane-m-dioxane.

It is also possible to use epoxy resins in which the epoxy groups are bonded to hetero atoms of various kinds or in which some or all of the epoxy groups are located in the centre of the molecule, such as the N,N,O-triglycidyl derivative of 4-aminophenol, N-glycidyl-N'-(2-glycidyloxypropyl)-5,5-dimethylhydantoin, vinylcyclohexene dioxide, limonene dioxide or dicyclopentadiene dioxide.

Said epoxy compounds can also be used in any mixtures with one another or with solid epoxy resins which are soluble in the epoxy resin mixture, the viscosity of the end mixture at room temperature being advantageously less than 15,000 mPa.s, preferably less than 8,000 mPa.s.

It is particularly preferable to use in the process according to the invention (so called) advanced or non-advanced

118

diglycidyl ethers of divalent phenols, especially of 2,2-bis-(4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)-propane, bis(4-hydroxyphenyl)methane, bis(4-hydroxycyclohexyl)methane and 2,2-bis(4-hydroxycyclohexyl)propane, poly-
5 glycidyl ethers of novolacs or tetraglycidylated 4,4'-diaminodiphenylmethane. It is even more preferable to use (so-called) advanced or non-advanced diglycidyl ethers of bisphenol A, tetrabromobisphenol A or bisphenol F, tetra-
glycidylated 4,4'-diaminodiphenylmethane, polyglycidyl
10 ethers of phenol-formaldehyde or cresol-formaldehyde novolacs, or mixtures thereof.

Said epoxy resins (b) can be mixed with a reactive diluent, for example phenyl or cresyl glycidyl ether, butanediol diglycidyl ether, diglycidyl hexahydrophthalate, neopen-
15 tyl glycol diglycidyl ether or glycidyl esters of synthetic highly branched, mainly tertiary aliphatic monocarboxylic acids known as "CARDURA E", preferably in an amount of 3-50% by weight based on the total amount of epoxy resins. o-Cresyl glycidyl ether is the preferred reactive diluent.

20 The binders to be used according to the invention can also contain further additives known per se, in particular thixotropes and dyes.

Salts (a) or the mixtures described above which are used in their place are advantageously used in such an amount
25 that there is 0.02 to 0.30, preferably 0.04 to 0.20 nitrogen equivalent per epoxy equivalent.

To ensure satisfactory impregnation of the laminate the viscosity of the binder at 25°C should not exceed
6,000 mPa.s, preferably 3,000 mPa.s and in particular
30 1,000 mPa.s. If necessary the desired value is set after all the binder components have been mixed by adding suitable diluents.

The binders to be used according to the invention (resin mixtures) are distinguished by a long shelf-life (up
35 to about 8 days at room temperature), so that it is possible to avoid premature curing of the resin during the preparation, any storage period and the transport of the laminates

49

impregnated therewith to the site of use. Said binders can be cured at low temperatures, generally at temperatures as low as 60°C, into coatings having good mechanical properties, such as good tensile and flexural strengths, and good resistance to chemicals. Furthermore, the linings or coatings obtained with the binders of the type defined feature low shrinkage and good adhesion to the substrate, i.e. the inner surfaces of the pipes, which are wet or at least moist in many cases owing to their intended use, their position or even the cleaning which preceded the relining. This is surprising, since mixtures of epoxy resins and commercially available salts of tertiary amines with organic acids generally do not give full curing in the presence of water or moisture and produce tacky coatings having inadequate mechanical properties.

The preparation of the laminates coated on one face with the binder of the type defined and lining of the pipes using the Insituform method can be carried out in a manner known per se. Suitable procedures, membrane materials and fibrous materials are described, for example, in British Patents 1,340,068 and 1,569,675, German Offenlegungsschriften 2,240,153 and 2,362,784 and the "Insituform News Digest" issued by the firm of Insituform (Pipes & Structures) Ltd., Great Britain. The relevant part of these publications is incorporated herein by reference. The membrane preferably consists of polyvinyl chloride sheeting, and the fibrous material is preferably polyester needle-punched felt.

The following Examples illustrate the invention.

A. Preparation of curing agents

Example 1: 265 g (1 mol) of tris(dimethylamino-methyl)phenol and 330 g (3 mol) of resorcinol are introduced into a 1.5 litre sulfonation flask which is equipped with a stirrer, a reflux condenser and a thermometer, and the mixture is heated with stirring in a nitrogen atmosphere to 110-120°C. At around 100°C the phenolic component dissolves in the amine. A mild exothermic reaction takes place. The temperature of the reaction mixture is held at 110-120°C

for 60 minutes. It is then diluted with 450 g of benzyl alcohol. This produces a pale brown solution having a viscosity of 5,600 mPa.s at 25°C, an OH equivalent: nitrogen equivalent ratio [eq. OH:eq. N] of 2:1, and a solids content of 57% by weight (curing agent No. 1).

Example 2: 68 g (1 mol) of imidazole and 272 g of benzyl alcohol are introduced at room temperature (20-25°C) into a 750 ml sulfonation flask which is equipped with a stirrer, a dropping funnel, a reflux condenser and a thermometer. The mixture is heated under a blanket of nitrogen to 100-110°C, and the imidazole dissolves to form a clear solution. 60 g of a technical bisphenol A diglycidyl ether (viscosity 10,000 mPa.s at 25°C, 5.35 epoxy equivalents/kg) are added dropwise at such a rate that 120°C is not exceeded. 200 g of a phenol novolac (OH equivalent weight = 105; 3.6 phenolic OH groups per mol) are then added, and the temperature is held at 110-120°C for about 60 minutes. The resulting product has a viscosity of 1,900 mPa.s at 25°C, an eq. OH:eq. N of 1:1, and a solids content of 55% by weight (curing agent No. 2).

Example 3: 100 g of bisphenol A [2,2-bis(4-hydroxyphenyl)propane] and 70 g of benzyl alcohol are introduced into a sulfonation flask of the type described in Example 1. The mixture is stirred under a blanket of nitrogen and is heated up to 110-120°C, and the bisphenol A dissolves to form a clear solution. 60 g of tris(dimethylaminomethyl)-phenol tris-2-ethylhexoate are then added, and the temperature of about 110°C is held for 30 minutes. The resulting curing agent (curing agent No. 3) has a viscosity of 7,200 mPa.s at 25°C and a solids content of 69% by weight.

Examples 4-36: The salts (curing agents) given in Table 1 below, are prepared analogously to the procedures described in Examples 1 and 2. Reaction conditions which differ from those of said Examples are likewise given in Table 1.

Table 1

Example (curing agent) No.	Salt of (g)	Diluent (g)	eq. Oil: eq. N	Viscosity at 25°C (mPa·s)	Solids content (% by weight)
4	Bisphenol A/Dimethylaminomethyl- phenol (228/151)	Benzyl alcohol (120)	2:1	12000	76
5	Bisphenol A/Dimethylaminomethyl- phenol (228/302)	Benzyl alcohol (100)	1:1	4700	84
6	Bisphenol A/Benzyl dimethylamine (228/135)	Benzyl alcohol (67)	2:1	13000	84
7	Bisphenol A/Benzyl dimethylamine (228/270)	Benzyl alcohol (22)	1:1	1200	96
8	Resorcinol/Dimethylaminomethyl- phenol (110/151)	Benzyl alcohol (100)	2:1	5300	72
9	Resorcinol/Dimethylaminomethyl- phenol (110/302)	Benzyl alcohol (60)	1:1	4100	85
10	Resorcinol/benzyl dimethylamine (110/135)	Benzyl alcohol (55)	2:1	1400	82

15

Table 1 (continued)

Example (curing agent) No.	Salt of (g)	Diluent (g)	eq. OH: eq. N	Viscosity at 25°C (mPa.s)	Solids con- tent (% by weight)
11	Resorcinol/Tris(dimethylamino- methyl)phenol (330/265)	Cyclohexanol (595)	2:1	8300	50
12	Resorcinol/Tris(dimethylamino- methyl)phenol (330/265)	Cyclohexanone (595)	2:1	680	50
13	Resorcinol/Tris(dimethylamino- methyl)phenol (330/265)	Furfuryl alcohol (595)	2:1	1300	50
14	Resorcinol/2-n-Propylimidazole (110/110)	Benzyl alcohol (70)	1:1	550	75
15	Resorcinol/2-n-Propylimidazole (220/110)	Benzyl alcohol (110)	2:1	1400	75
16	Resorcinol/N,N-Diethylamino- propylamine (110/130)	Benzyl alcohol (80)	1:1	2900	75
17	Resorcinol/N,N-Dimethylamino- propylamine (220/98)	Benzyl alcohol (166)	2:1	9100	66

52

Table 1 (continued)

Example (curing agent) No.	Salt of (g)	Diluent (g)	eq. OH: eq. N	Viscosity at 25°C (mPa·s)	Solids con- tent (% by weight)
18	Bisphenol A/N,N-Diethylamino- propylamine (228/130)	Benzyl alcohol (212)	1:1	1000	63
19	Bisphenol A/N,N-Diethylamino- propylamine (456/130)	Benzyl alcohol (384)	2:1	2600	60
20	Bisphenol A/N,N-Dimethylamino- propylamine (228/98)	Benzyl alcohol (214)	1:1	800	60
21	Bisphenol A/2-n-Propylimidazole (228/110)	Benzyl alcohol (222)	1:1	360	60
22	Novolac ¹⁾ /2-n-Propylimidazole (200/110)	Benzyl alcohol (200)	1:1	1000	61
23	Novolac ¹⁾ /2-n-Propylimidazole (400/110)	Benzyl alcohol (330)	2:1	2400	61
24	Novolac ¹⁾ /2-n-Propylimidazole (200/220)	Benzyl alcohol (180)	1:2	1000	70

Table 1 (continued)

Example (curing agent) No.	Salt of (g)	Diluent (g)	eq. Oil: eq. N	Viscosity at 25°C (mPa·s)	Solids con- tent (% by weight)
25	Novolac 1)/Imidazole (400/68)	Benzyl alcohol (302)	2:1	3100	61
26	Novolac 1)/2-n-Propylimidazole Imidazole (400/110/68), Imid- azole prereacted with 60 g of bisphenol A diglycidyl ether as in Example 2	Benzyl alcohol (412)	1:1	2500	61
27	Resorcinol/Imidazole (110/68), Imidazole prereacted with 60 g of bisphenol A diglycidyl ether as in Example 2	Benzyl alcohol (238)	1:1	260	50
28	Resorcinol  -C(=O)-NH(CH ₂) ₃ N(C ₂ H ₅) ₂ (110/234)	Benzyl alcohol (146)	1:1	3200	70
29	Resorcinol  -C(=O)-NH(CH ₂) ₃ N(C ₂ H ₅) ₂ (220/234)	Benzyl alcohol (196)	2:1	14500	70

Table 1 (continued)

Example (curing agent) No.	Salt of (g)	Diluent (g)	eq. OH: eq. N	Viscosity at 25°C (mPa·s)	Solids con- tent (% by weight)
30	 Resorcinol $\text{N}(\text{C}_2\text{H}_5)_2$ (110/468)	Benzyl alcohol (252)	1:2	530	70
31	Resorcinol/2-n-Propylimidazole	-	2:1	82000	100
32	3-(2,4,6-Pentadecatrienyl)phenol [Phenol CNSL ²]/Tris(dimethylamino- methyl)phenol (670/265)	-	2:3	1200	100
33	do. (1005/265)	-	3:3	1000	100
34	4-n-Nonylphenol/Tris(dimethyl- aminomethyl)phenol (666/265)	-	3:3	14700	100
35	Phenol CNSL/2-n-Propylimidazole (335/110)	-	1:2	200	100
36	4-n-Nonylphenol/2-n-Propyl- imidazole (444/110)	-	2:2	1400	100

1) Phenol novolac having an OH equivalent weight of 105; 3.6 phenolic OH groups per mol.

2) Phenol extracted from cashew nuts

56

2:1 Salts of resorcinol and 2-n-propylimidazole can be prepared as follows:

a) without added diluent (curing agent No. 31)

330 g (3 mol) of 2-n-propylimidazole are introduced into a 1.5 litre sulfonation flask which is equipped with a condenser, a stirrer, a thermometer and a wide-stemmed funnel. The compound is stirred under a blanket of nitrogen and is heated to about 100°C by means of a heatable oil bath. 660 g (6 mol) of resorcinol are then added. There is a distinct exothermic reaction. After the exothermic reaction has died down the product is maintained at 120°C for about one more hour. It is then cooled down. The salt obtained is a dark brown clear highly viscous liquid having an amine content of 3.2 equivalents/kg, a Höppler viscosity at 25°C of 82,000 mPa s, a density at 25°C of 1.193 g/cm³, and a refractive index at 25°C of 1.572.

b) with added benzyl alcohol (curing agent No. 15)

440 g (4 mol) of resorcinol and 220 g of benzyl alcohol are introduced into a 1.5 litre sulfonation flask which is equipped with a condenser, a stirrer, a thermometer and a dropping cylinder. The mixture is heated with stirring in an inert gas atmosphere by means of a heatable oil bath to about 100-120°C, and all of the resorcinol dissolves. 220 g (2 mol) of 2-n-propylimidazole are then added, and there is a marked exothermic reaction. The 2-n-propylimidazole is added at such a rate that the temperature does not exceed 130°C. After the exothermic reaction has died down the product is held at 130°C for about one more hour. It is then cooled down. The result is a clear brown solution of the 2:1 resorcinol/2-n-propylimidazole salt having an amine content of 2.4 equivalents/kg, a viscosity at 25°C of 1,400 mPa s, a density at 25°C of 1.149 g/cm³, and a refractive index at 25°C of 1.5620.

Examples 37-45: The procedure described in Example 3 is used to prepare the curing agents given in Table 2, below. Reaction conditions which differ from those of Example 3 are likewise given in Table 2.

57

Table 2

Example (curing agent) No.	Curing agent of (g)	Diluent (g)	Viscosity 25°C (mPa.s)	Solids content (% by weight)
37	Resorcinol/Tris(dimethylamino- methyl)phenol 2-ethylhexoate (50/100)	Benzyl alcohol (50)	5800	75
38	Resorcinol/Tris(dimethylamino- methyl)phenol 2-ethylhexoate (50/100)	Benzyl alcohol (100)	620	60
39	Resorcinol/Tris(dimethylamino- methyl)phenol 2-ethylhexoate (100/60)	Benzyl alcohol (90)	1200	64
40	Resorcinol/Tris(dimethylamino- methyl)phenol 2-ethylhexoate (100/80)	Benzyl alcohol (70)	4700	72
41	Bisphenol A/Tris(dimethyl- aminomethyl)phenol tris-2- ethylhexoate (100/60)	Benzyl alcohol (90)	2400	64

Table 2 (continued)

Example (curing agent) No.	Curing agent of (g)	Diluent (g)	Viscosity 25°C (mPa·s)	Solids content (% by weight)
42	Bisphenol A/Tris(dimethyl-aminomethyl)phenol tris-2-ethylhexoate (150/80)	Benzyl alcohol (120)	3600	66
43	Bisphenol A/Tris(dimethyl-aminomethyl)phenol tris-2-ethylhexoate (50/60)	Benzyl alcohol (40)	5600	73
44	Bisphenol A/Tris(dimethyl-aminomethyl)phenol tris-2-ethylhexoate (150/60)	Benzyl alcohol (100)	5500	67
45	Bisphenol A/Tris(dimethyl-aminomethyl)phenol tris-2-ethylhexoate (100/60)	Benzyl alcohol (50)	35000	76

B. Application Examples

Examples 46-89: Resin and curing agent are mixed by hand in a beaker in the amounts indicated in Table 3. The viscosity of the freshly prepared mixtures is then determined. In all the Examples the resin is 100 g of a mixture of 73% by weight of a bisphenol A diglycidyl ether (viscosity at 25°C 10,000-12,000 mPa.s, 5.25-5.4 epoxy equivalents/kg) and 27% by weight of o-cresyl glycidyl ether (reactive diluent).

In each Example, four layers of a 3 mm thick felt (a 15 x 20 cm polyester needle-punched felt) are separately impregnated with the resin/curing agent mixture. The four layers of the impregnated felt are then pressed in a moulding press into 12 mm thick test specimens. The moulding press is subsequently placed into a basin which contains cold water and which is surrounded by a second basin, which is filled with an oil bath. The oil bath is heated to 70°C, which has the effect of raising the temperature of the water in the inner basin to 60°C. The water bath is held at 60°C for 5 hours. The oil bath heating is then switched off and the oil bath is allowed to cool down overnight. The next morning the moulding press is taken out of the water and the test specimens are removed from the moulding press. The test specimens are measured for the following properties:

- tensile strength (max) in accordance with ISO 3268 (International Standards Organisation) in N/mm²,
- flexural strength (max) in accordance with ASTM D 790 in N/mm²
- modulus of elasticity in accordance with ISO 3268 in N/mm².

Also tested is the shelf-life of the impregnated felts (3 mm thick) at 20°C, in terms of the increasing stiffness of the felt, i.e. until the latter is no longer kneadable by hand.

The experimental arrangement described above meets to a very high degree of approximation the practical conditions of lining inner surfaces of pipes by the Insituform method.

- 25 -

The results of the experiments have been collated in Table 3, below.

Table 3

Exam- ple No.	Resin mixture of 100 g of resin/x g of curing agent No.	Viscosity of resin/curing agent mixture 25°C/mPa.s	Shelf-life 20°C/ (days)	Tensile strength by ISO 3268 N/mm ²	Flexural strength by ASTM D ₂₇₉₀ N/mm	Modulus of elasticity by ISO 3268 N/mm
46	10 g curing agent No. 1	700	6	39	63	3530
47	15 g curing agent No. 2	600	5	37	62	3500
48	23 g curing agent No. 3	670	8	38	66	3100
49	10 g curing agent No. 4	620	6	43	66	3600
50	10 g curing agent No. 5	670	3	49	68	3900
51	10 g curing agent No. 6	650	2	40	59	3400
52	10 g curing agent No. 8	550	6	43	67	3800
53	10 g curing agent No. 9	540	3	44	67	3700
54	10 g curing agent No. 10	610	1	46	61	3700
55	12 g curing agent No. 11	600	6	41	71	3400

66

Table 3 (continued)

Exam- ple No.	Resin mixture of 100 g of resin/x g of curing agent No.	Viscosity of resin/curing agent mixture 25°C/mPa·s	Shelf-life 20°C/(days)	Tensile strength by ISO 3268 N/mm ²	Flexural strength by ASTM D ₂₇₉₀ N/mm	Modulus of elasticity by ISO 3268 N/mm ²
56	12 g curing agent No.12	600	7	40	73	3400
57	12 g curing agent No.13	550	5	38	61	3600
58	10 g curing agent No.14	560	4	41	65	3500
59	10 g curing agent No.15	560	6	38	54	3200
60	7 g curing agent No.16	500	5	44	72	3500
61	10 g curing agent No.17	700	6	49	72	3800
62	10 g curing agent No.18	460	4	40	62	3300
63	20 g curing agent No.19	500	5	41	73	3400
64	12 g curing agent No.21	620	3	37	61	3300
65	15 g curing agent No.21	430	4	42	63	3600

Table 3 (continued)

Exam- ple No.	Resin mixture of 100 g of resin/x g of curing agent No.	Viscosity of resin/curing agent mixture 25°C/mPa.s	Shelf-life 20°C (days)	Tensile strength by ISO 2 3268 N/mm ²	Flexural strength by ASTM D 2790 N/mm	Modulus of elasticity by ISO 3268 N/mm
66	10 g curing agent No.22	550	5	39	63	3500
67	10 g curing agent No.23	640	4	39	71	3500
68	10 g curing agent No.24	540	4	37	62	3500
69	15 g curing agent No.25	670	5	38	63	3600
70	15 g curing agent No.26	610	4	39	62	3700
71	12 g curing agent No.27	470	5	32	50	3600
72	20 g curing agent No.37	600	7	38	66	3380
73	25 g curing agent No.38	450	7	37	63	2850
74	25 g curing agent No.39	550	13	37	65	3100
75	25 g curing agent No.40	700	8	37	66	3330

64

Table 3 (continued)

Exam- ple No.	Resin mixture of 100 g of resin/x g of curing agent No.	Viscosity of resin/curing agent mixture 25°C/mPa.s	Shelf-life 200°C (days)	Tensile strength by ISO 2 3268 N/mm ²	Flexural strength by ASTM D ₂ 790 N/mm ²	Modulus of elasticity by ISO 3268 N/mm ²
76	25 g curing agent No.41	550	1)	39	68	3000
77	35 g curing agent No.42	570	1)	34	63	2650
78	15 g curing agent No.43	600	8	37	65	3240
79	31 g curing agent No.44	650	1)	35	67	2900
80	21 g curing agent No.45	710	8	35	65	3000
81	20 g curing agent No.28	600	3	35	51	3600
82	20 g curing agent No.29	800	5	38	58	3350
83	20 g curing agent No.30	400	2	32	50	2800
84	7.5 g curing agent No.31	1000	6	41	58	3500

1) not determined.

Table 3 (continued)

Exam- ple No.	Resin mixture of 100 g of resin/x g of curing agent No.	Viscosity of resin/curing agent mixture 25°C/mPa.s	Shelf-life 20°C (days)	Tensile strength by ISO 2 3268 N/mm ²	Flexural strength by ASTM D ₂ 790 N/mm	Modulus of elasticity by ISO 3268 N/mm ²
85	12 g curing agent No.32	600	3	29	53	2900
86	10 g curing agent No.33	600	6	31	47	2700
87	10 g curing agent No.34	600	2	35	54	3300
88	20 g curing agent No.35	400	3	34	63	2800
89	10 g curing agent No.36	600	5	30	56	3250

1) not determined.

66

Examples 90-100: The method described in Examples 46-89 is used to test further resin/curing agent mixtures in which the following resins are used:

5 Resin I: Mixture of 70% by weight of bisphenol A diglycidyl ether having 5.25-5.4 epoxy equivalents/kg and 30% by weight of bisphenol F diglycidyl ether having 5.7 epoxy equivalents/kg.

Resin II: Bisphenol A diglycidyl ether having 5.25-5.4 epoxy equivalents/kg.

10 Resin III: Mixture of 50% by weight of bisphenol A diglycidyl ether having 5.25-5.4 epoxy equivalents/kg and 50% by weight of distilled bisphenol F diglycidyl ether having 6.1 epoxy equivalents/kg.

15 Resin IV: Mixture of 94% by weight of bisphenol A diglycidyl ether having 5.25-5.4 epoxy equivalents/kg and 6% by weight of o-cresyl glycidyl ether.

Resin V: Bisphenol F diglycidyl ether having 5.7 epoxy equivalents/kg.

20 Resin VI: Distilled bisphenol F diglycidyl ether having 6.1 epoxy equivalents/kg.

Resin VII: Mixture of 90% by weight of Resin I and 10% by weight of a mixture of n-dodecyl and n-tetradecyl glycidyl ethers having 3.4 epoxy equivalents/kg.

25 Resin VIII: Mixture of 90% by weight of bisphenol A diglycidyl ether having 5.25-5.4 epoxy equivalents/kg and 10% by weight of a mixture of n-dodecyl and n-tetradecyl glycidyl ethers having 3.4 epoxy equivalents/kg.

30 Resin IX: Mixture of 78% by weight of bisphenol A diglycidyl ether having 5.25-5.4 epoxy equivalents/kg and 22% by weight of neopentylglycol diglycidyl ether having 7.2 epoxy equivalents/kg.

The results have been collated in Table 4, below.

Table 4

Exam- ple No.	Resin mixture of 100 g of resin/x g of curing agent No.	Viscosity of resin/curing agent mixture 25°C/mPa.s	Shelf-life 20°C (days)	Tensile strength by ISO 3268 N/mm ²	Flexural strength by ASTM D 790 N/mm ²	Modulus of elasticity by ISO 3268 N/mm ²
90	100 g Resin I/10 g curing agent No. 15	6500	3	46	82	3500
91	100 g Resin II/10 g curing agent No. 15	6800	3	45	64	3700
92	100 g Resin III/10 g curing agent No. 15	3300	3	38	61	3500
93	100 g Resin IV/10 g curing agent No. 15	4000	3	38	67	3750
94	100 g Resin V/10 g curing agent No. 15	4300	3	45	72	3500
95	100 g Resin VI/10 g curing agent No. 15	1500	5	37	58	3400
96	100 g Resin VII/10 g curing agent No. 15	1600	5	40	60	3000

Table 4 (continued)

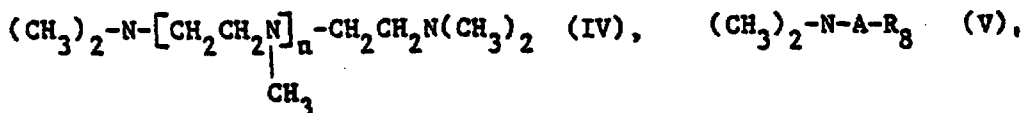
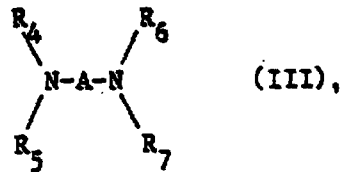
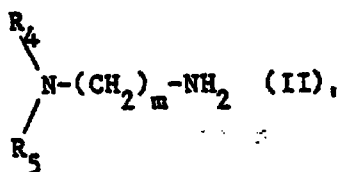
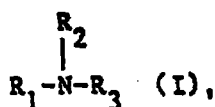
Exam- ple No.	Resin mixture of 100 g of resin/x g of curing agent No.	Viscosity of resin/curing agent mixture 25°C/mPa·s	Shelf-life 20°C (days)	Tensile strength by ISO 3268 N/mm ²	Flexural strength by ASTM D 790 N/mm ²	Modulus of elasticity by ISO 3268 N/mm ²
97	100 g Resin I/10 g curing agent No. 14	6000	1	50	66	3770
98	100 g Resin IV/10 g curing agent No. 14	4600	1	44	69	3700
99	100 g Resin VIII/10 g curing agent No. 14	2300	2	44	70	3500
100	100 g Resin IX/10 g curing agent No. 14	1100	2	45	76	3500

69

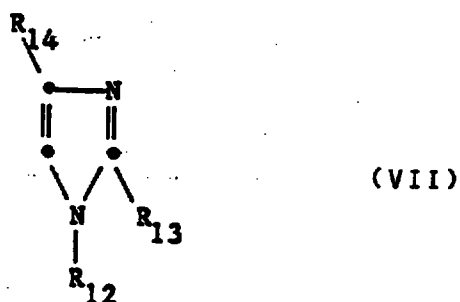
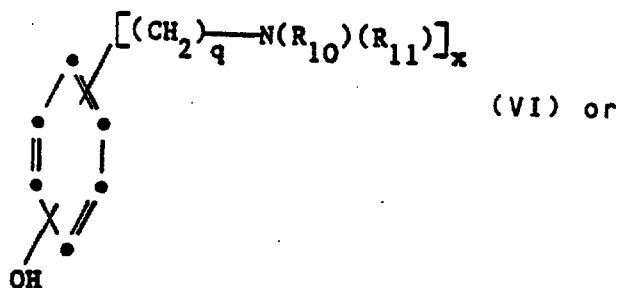


Claims:

1. A process for lining the inner surfaces of pipes or pipe sections by the Insituform method by pressing a tubular flexible laminate made up of an essentially liquid-impermeable membrane and a fibrous layer which has been impregnated with a binder which is not as yet fully cured with the face with the binder against the inner surface of the pipe by means of liquid pressure in such a way that the laminate takes on the shape of the inner surface of the pipe and the binder becomes fully cured in this state, forming a firmly adhering internal lining, which comprises using a laminate which has been impregnated with a binder which contains
 - (a) a curing agent which is a salt of one or more (poly)-amines having at least one tertiary nitrogen atom and one or more aromatic polyols or one or more aliphatically substituted phenols, the aliphatic radical having at least 9 carbon atoms, and
 - (b) a liquid epoxy resin or a liquid mixture of epoxy resins.
2. A process according to Claim 1, wherein the amine in curing agent (a) is an amine of formulae I to VII



78



in which m is 2-6, n is zero, 1 or 2,
 R_1 is C_{1-12} -alkyl, hydroxyalkyl having 1-4 carbon atoms or alkoxyalkyl having a total of 2-6 carbon atoms,
 R_2 and R_3 , independently of the other, are each the same as R_1 or are each unsubstituted or substituted phenyl, benzyl, phenylethyl, cyclopentyl or cyclohexyl,
 R_4 is C_{1-4} -alkyl,
 R_5 is C_{1-4} -alkyl, cyclopentyl or cyclohexyl,
 R_6 is C_{1-12} -alkyl, phenyl, benzyl, phenylethyl, benzoyl, cyclopentyl, cyclohexyl, $-A_1CN$ or $-A_1CH_2NH_2$,
 R_7 is hydrogen or $-A_1CH_2NH_2$ or
 R_6 and R_7 together are $-(CH_2)_p-$ with $p = 4$ or 5 ,
 $-(CH_2)_2O(CH_2)_2-$ or $-(CH_2)_2NH(CH_2)_2-$,
 R_8 is $-OR_9$, $-O\overset{\overset{O}{\parallel}}{C}R_9$, $-O\overset{\overset{O}{\parallel}}{C}NHR_9$, $-O-A_1CN$, $-O-A_1NH_2$, $-O\overset{\overset{O}{\parallel}}{C}-A_1-N-$
 $(CH_3)_2$, $-O\overset{\overset{O}{\parallel}}{C}-Y-\overset{\overset{O}{\parallel}}{C}O-A_1-N(CH_3)_2$ or $-O-Y_1-O-A_1-N(CH_3)_2$,
 R_9 is C_{1-12} -alkyl, phenyl, benzyl, cyclopentyl or cyclohexyl,
 R_{10} and R_{11} , independently of the other, are each C_{1-4} -alkyl,
 R_{12} is hydrogen, C_{1-4} -alkyl, phenyl or benzyl and
 R_{13} and R_{14} , independently of the other, are each hydrogen,



- 36 -

a halogen atom, C_{1-4} -alkyl, phenyl, cyclohexyl or benzyl, A and A_1 , independently of the other, are each ethylene or 1,2- or 1,3-propylene,

Y is a direct bond, $-C_rH_{2r}-$ with $r = 2-10$, phenylene, toluylene or cyclohexylene,

Y_1 is $-C_rH_{2r}-$ with $r = 2-10$, phenylene, toluylene or cyclohexylene,

q is 1 or 2 and x is 1-3.

3. A process according to Claim 2, wherein the amine is an adduct of an imidazole of the formula VII in which R_{12} is hydrogen and R_{13} and R_{14} are as defined in Claim 2 with a diglycidyl ether of an aromatic polyol, in particular a diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane [bisphenol A], 2,2-bis(4-hydroxycyclohexyl)propane [hydrogenated bisphenol A] or bis(4-hydroxyphenyl)methane [bisphenol F].

4. A process according to Claim 2, wherein the amine is N,N-dimethyl-N'-(3-aminopropyl)-1,3-diaminopropane, N,N-dimethyl-N'-(2-cyanoethyl)-1,3-diaminopropane or N,N-diethyl-N'-(benzoyl)-1,3-diaminopropane or a mixture thereof or a compound of the formula I, II, VI or VII where R_1 and R_2 are each ethyl or methyl, R_3 is unsubstituted phenyl or unsubstituted benzyl, m is 2 or 3, R_4 and R_5 , independently of the other, are each methyl or ethyl, q is 1, R_{10} and R_{11} are both ethyl or are both methyl, R_{12} and R_{14} are each hydrogen, R_{13} is hydrogen or C_{1-4} -alkyl and x is as defined in Claim 2.

5. A process according to Claim 2, wherein the amine is an adduct of imidazole and a diglycidyl ether of bisphenol F, hydrogenated bisphenol A or bisphenol A.

6. A process according to Claim 1, wherein the polyol in curing agent component (a) is resorcinol, hydroquinone, bisphenol F, bisphenol A, 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 4,4'-dihydroxybiphenyl, bis(4-hydroxyphenyl) sulfone or a novolac of formaldehyde or acetaldehyde and phenol, chlorophenol or an alkylphenol having up to 9 carbon atoms in the alkyl.

7. A process according to Claims 1-5, wherein the polyol in curing agent component (a) is a phenol novolac, resorcinol, bisphenol F or bisphenol A.

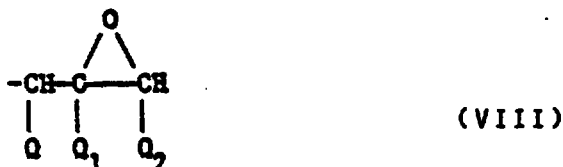


72

8. A process according to Claim 1, wherein curing agent component (a) is a salt of resorcinol, bisphenol F or bisphenol A and tris(dimethylaminomethyl)phenol, dimethylaminomethylphenol, 2-n-propylimidazole, N,N-dimethylaminopropylamine, N,N-diethylaminopropylamine or N,N-diethyl-N'-(benzoyl)-1,3-diaminopropane or a salt of resorcinol, bisphenol F or bisphenol A and an adduct of imidazole and a diglycidyl ether of bisphenol A or bisphenol F.

9. A process according to Claim 1, wherein curing agent component (a) is a salt in which there are 1 to 2 OH equivalents per nitrogen equivalent.

10. A process according to Claim 1, wherein component (b) is an epoxy resin having on average more than one group which is bonded to a hetero atom and has the formula VIII



in which Q and Q₂ are both hydrogen atoms and Q₁ is a hydrogen atom or a methyl group or Q and Q₂ together are -CH₂CH₂- or -CH₂CH₂CH₂- and Q₁ is a hydrogen atom.

11. A process according to Claim 1, wherein component (b) is a (so-called) advanced or non-advanced diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane [tetrabromobisphenol A], bis(4-hydroxyphenyl)methane, bis(4-hydroxycyclohexyl)methane or 2,2-bis(4-hydroxycyclohexyl)propane, a polyglycidyl ethers of novolacs or tetraglycidylated 4,4'-diaminodiphenylmethane.

12. A process according to Claim 1, wherein component (b) is a (so-called) advanced or non-advanced diglycidyl ether of bisphenol A, tetrabromobisphenol A or bisphenol F, tetraglycidylated 4,4'-diaminodiphenylmethane, a polyglycidyl ether of a phenol-formaldehyde or cresol-formaldehyde novolac or a mixture thereof.

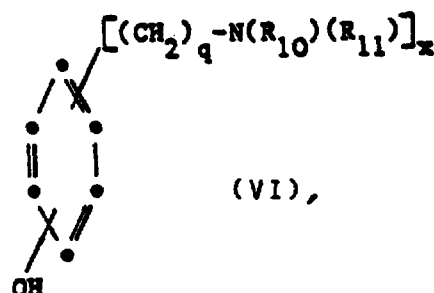
13. A process according to Claim 1, wherein the further additive (c) is a reactive diluent for component (b).

14. A modified process according to Claim 1, wherein curing agent (a) is a mixture of aromatic diols and salts of



73

compounds of the formula VI



in which q is 1 or 2, x is 1-3, and R_{10} and R_{11} , independently of the other, are each C_{1-4} -alkyl, with saturated or unsaturated, straight-chain or branched aliphatic monocarboxylic acids.

15. A process according to Claim 14, wherein a mixture of bisphenol A or bisphenol F and dimethyl-aminomethylphenol 2-ethylhexoate or oleate or tris(dimethylaminomethyl)phenol tris-2-ethylhexoate is used.

16. A process according to Claim 1 or 14, wherein curing agent component (a) is used in such an amount that there is 0.02 to 0.30, in particular 0.04 to 0.20, nitrogen equivalent per epoxy equivalent of component (b).

17. A process according to Claim 1 or 14, wherein the viscosity of the binder at 25°C does not exceed 6,000 mPa.s, in particular 3,000 mPa.s.

18. Salts of resorcinol or bisphenol A and dimethyl-aminomethylphenol, tris(dimethylaminomethyl)phenol or 2-n-propylimidazole, salts of a phenol novolac and imidazole, 2-n-propylimidazole or an adduct of imidazole and a bisphenol A diglycidyl ether and salts of resorcinol or bisphenol A and an adduct of imidazole and a bisphenol A diglycidyl ether.



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Claims

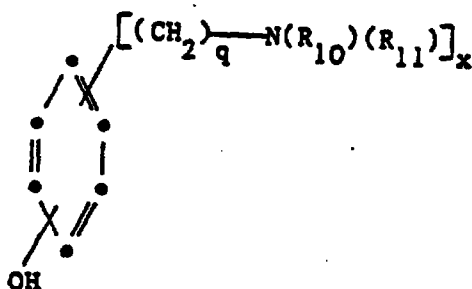
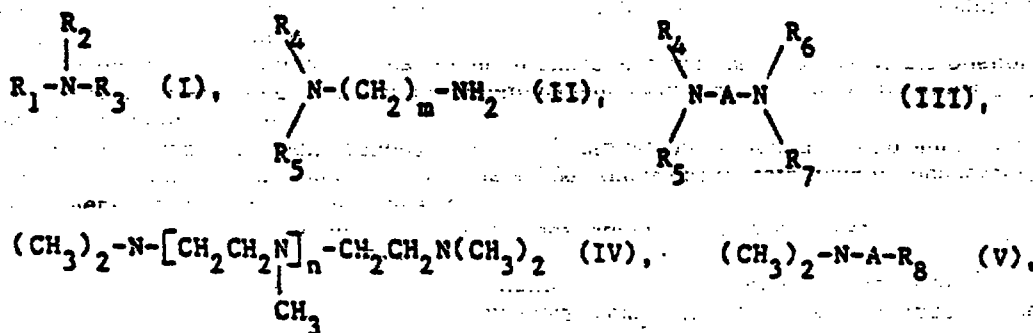
1. A process for lining the inner surfaces of pipes or pipe sections using the Insituform method by pressing a tubular flexible laminate made up of an essentially liquid-impermeable membrane and a fibrous layer which has been impregnated with a binder which is not as yet fully cured with the face with the binder against the inner surface of the pipe by means of liquid pressure in such a way that the laminate takes on the shape of the inner surface of the pipe and the binder becomes fully cured in this state, forming a firmly adhering internal lining, which comprises using a laminate which has been impregnated with a binder which contains

(a) a curing agent which is a salt of one or more (poly)amines having at least one tertiary nitrogen atom and one or more aromatic polyols or one or more aliphatically substituted phenols, the aliphatic radical having at least 9 carbon atoms, and

(b) a liquid epoxy resin or a liquid mixture of epoxy resins and can, if desired, also contain

(c) further additives.

2. A process according to Claim 1, wherein the amine in curing agent (a) is an amine of formulae I to VII

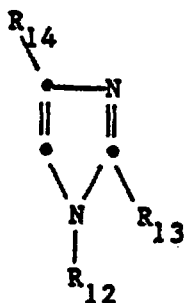


(VI) or



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(VII)

in which m is 2-6, n is zero, 1 or 2;

R₁ is C₁₋₁₂-alkyl, hydroxyalkyl having 1-4 carbon atoms or alkoxyalkyl having a total of 2-6 carbon atoms,

R₂ and R₃, independently of the other, are each the same as R₁ or are each unsubstituted or substituted phenyl, benzyl, phenylethyl, cyclopentyl or cyclohexyl,

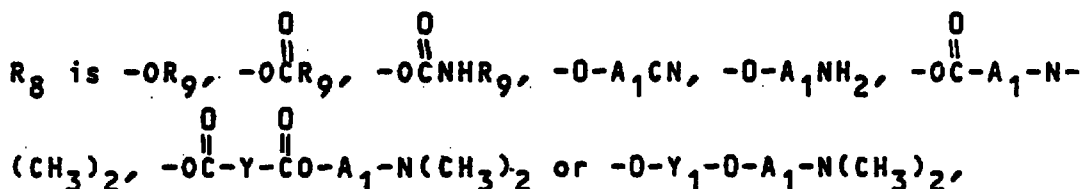
R₄ is C₁₋₄-alkyl,

R₅ is C₁₋₄-alkyl, cyclopentyl or cyclohexyl,

R₆ is C₁₋₁₂-alkyl, phenyl, benzyl, phenylethyl, benzoyl, cyclopentyl, cyclohexyl, -A₁CN or -A₁CH₂NH₂,

R₇ is hydrogen or -A₁CH₂NH₂ or

R₆ and R₇ together are -(CH₂)_p- with p = 4 or 5, -(CH₂)₂O(CH₂)₂- or -(CH₂)₂NH(CH₂)₂-.



R₉ is C₁₋₁₂-alkyl, phenyl, benzyl, cyclopentyl or cyclohexyl,

R₁₀ and R₁₁, independently of the other, are each C₁₋₄-alkyl,

R₁₂ is hydrogen, C₁₋₄-alkyl, phenyl or benzyl and

R₁₃ and R₁₄, independently of the other, are each hydrogen, a halogen atom, C₁₋₄-alkyl, phenyl, cyclohexyl or benzyl, A and A₁, independently of the other, are each ethylene or 1,2- or 1,3-propylene,

Y is a direct bond, -C_rH_{2r}- with r = 2-10, phenylene, toluylene or cyclohexylene,

Y₁ is -C_rH_{2r}- with r = 2-10, phenylene, toluylene or cyclohexylene,

q is 1 or 2 and x is 1-3.

3. A process according to Claim 2, wherein the amine is an adduct of an imidazole of the formula VII in which R₁₂ is hydrogen and R₁₃ and R₁₄ are as defined in Claim 2 with a diglycidyl ether of an aromatic polyol, in particular a diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane [bisphenol A], 2,2-bis(4-hydroxycyclohexyl)propane [hydrogenated bisphenol A] or bis(4-hydroxyphenyl)methane [bisphenol F].

4. A process according to Claim 2, wherein the amine is N,N-dimethyl-N'-(3-aminopropyl)-1,3-diaminopropane, N,N-di-methyl-N'-(2-cyanoethyl)-1,3-diaminopropane or N,N-diethyl-N'-(benzoyl)-1,3-diaminopropane or a mixture thereof or a compound of the formula I, II, VI or VII where R₁ and R₂ are each ethyl or methyl, R₃ is unsubstituted phenyl or unsubstituted benzyl, m is 2 or 3, R₄ and R₅, independently of the other, are each methyl or ethyl, q is 1, R₁₀ and R₁₁ are both ethyl or are both methyl, R₁₂ and R₁₄ are each hydrogen, R₁₃ is hydrogen or C₁₋₄-alkyl and x is as defined in Claim 2.

5. A process according to Claim 2, wherein the amine is an adduct of imidazole and a diglycidyl ether of bisphenol F, hydrogenated bisphenol A or bisphenol A.

6. A process according to Claim 1, wherein the polyol in curing agent component (a) is resorcinol, hydroquinone, bisphenol F, bisphenol A, 2,2-bis(4-hydroxy-3,5-dibromophenyl)-propane, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 4,4'-dihydroxybiphenyl, bis(4-hydroxyphenyl) sulfone or a novolac of formaldehyde or acetaldehyde and phenol, chlorophenol or alkylphenol having up to 9 carbon atoms in the alkyl.

7. A process according to Claims 1-5, wherein the polyol in curing agent component (a) is a phenol novolac, resorcinol, bisphenol F or bisphenol A.

8. A process according to Claim 1, wherein curing agent component (a) is a salt of resorcinol, bisphenol F or bisphenol A and tris(dimethylaminomethyl)phenol, dimethylaminomethylphenol, 2-n-propylimidazole, N,N-dimethylaminopropylamine, N,N-diethylaminopropylamine or N,N-diethyl-N'-(benzoyl)-1,3-diaminopropane or a salt of resorcinol, bisphenol F or bisphenol A and an adduct of imidazole and a diglycidyl ether of bisphenol A or bisphenol F.

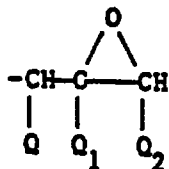
9. A process according to Claim 1, wherein curing agent component (a) is a salt in which there are 1 to 2 OH equivalents per nitrogen equivalent.



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according to Claim 1, wherein component (b) is an epoxy resin having on average more than which is bonded to a hetero atom and has the formula VIII



(VIII)

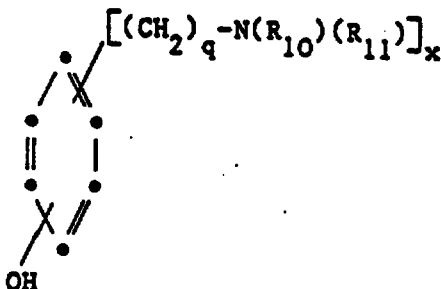
in which Q and Q₂ are both hydrogen atoms and Q₁ is a hydrogen atom or a methyl group or Q and Q₂ together are -CH₂CH₂- or -CH₂CH₂CH₂- and Q₁ is a hydrogen atom.

11. A process according to Claim 1, wherein component (b) is a (so-called) advanced or non-advanced diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane [tetrabromobisphenol A], bis(4-hydroxyphenyl)methane, bis(4-hydroxycyclohexyl)methane or 2,2-bis(4-hydroxycyclohexyl)propane, a polyglycidyl ether of a novolac or tetraglycidylated 4,4'-diaminodiphenylmethane.

12. A process according to Claim 1, wherein component (b) is a (so-called) advanced or non-advanced diglycidyl ether of bisphenol A, tetrabromobisphenol A or bisphenol F, tetraglycidylated 4,4'-diaminodiphenylmethane, a polyglycidyl ether of a phenol-formaldehyde or cresol-formaldehyde novolac or a mixture thereof.

13. A process according to Claim 1, wherein the further additive (c) is a reactive diluent for component (b).

14. A modified process according to Claim 1, wherein curing agent (a) is a mixture of aromatic diols and salts of compounds of the formula VI



(VI)

in which q is 1 or 2, x is 1-3, and R₁₀ and R₁₁, independently of the other, are each C₁₋₄-alkyl, with unsaturated or saturated, straight-chain or branched aliphatic monocarboxylic acids.

15. A process according to Claim 14, wherein a mixture of bisphenol A or bisphenol F and dimethylaminomethylphenol 2-ethylhexoate or oleate or tris(dimethylaminomethyl)phenol tris-2-ethylhexoate is used.

16. A process according to Claim 1 or 14, wherein curing agent component (a) is used in such an amount that there is 0.02 to 0.30, in particular 0.04 to 0.20, nitrogen equivalent per epoxy equivalent of component (b).

17. A process according to Claim 1 or 14, wherein the viscosity of the binder at 25°C does not exceed 6,000 mPa.s, in particular 3,000 mPa.s.

18. Salts of resorcinol or bisphenol A and dimethylaminomethylphenol, tris(dimethylaminomethyl)phenol or 2-n-propylimidazole, salts of a phenol novolac and imidazole, 2-n-propylimidazole or an adduct of imidazole and a bisphenol A diglycidyl ether and salts of resorcinol or bisphenol A and an adduct of imidazole and a bisphenol A diglycidyl ether.

Revendications

1. Procédé pour revêtir intérieurement des tubes ou des parties de tubes par la méthode "Insituform", selon lequel un stratifié souple en forme de tuyau, constitué d'une membrane pratiquement imperméable aux liquides et d'une couche fibreuse imprégnée d'un liant non encore durci, est appliqué, au moyen d'un liquide sous pression, par son côté portant le liant, contre la surface intérieure du tube de telle façon que le stratifié prenne la forme de la surface intérieure du tube, et le liant est durci dans cet état en donnant un revêtement intérieur adhérent, ce procédé étant caractérisé en ce qu'on utilise un stratifié imprégné d'un liant qui contient:

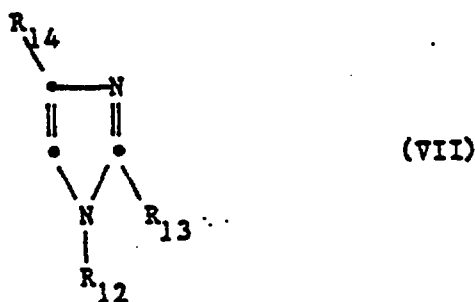
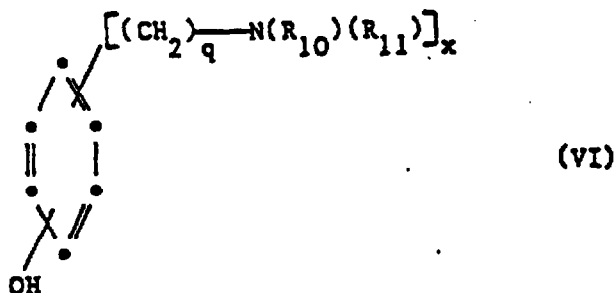
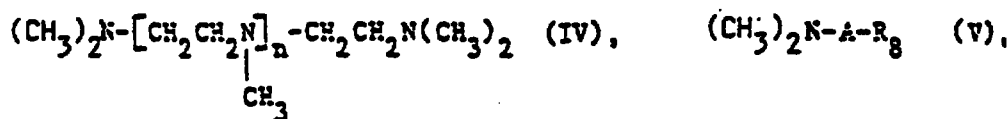
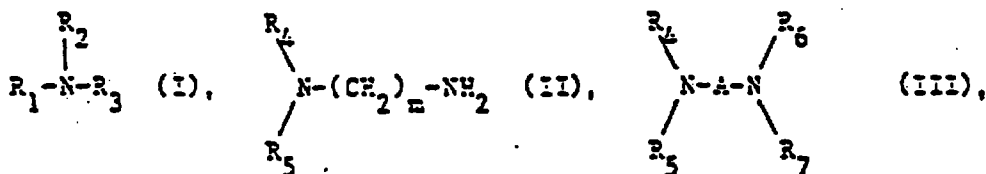
(a) comme durcisseur un sel dérivant d'une ou plusieurs (poly)amines renfermant au moins un atome d'azote tertiaire et d'un ou plusieurs polyols aromatiques ou d'un ou plusieurs phénols porteurs d'un radical



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ce radical aliphatique contenant au moins 9 atomes de carbone, et
résine époxydique liquide ou un mélange liquide de résines époxydiques.
défini selon la revendication 1 caractérisé en ce que l'amine, dans le durcisseur (a), est une amine
conformément à l'une des formules I à VII:



dans lesquelles:

m représente un nombre de 2 à 6,

n représente un nombre égal à 0, à 1 ou à 2,

R₁ représente un alkyle en C₁-C₁₂, un hydroxyalkyle en C₁-C₄ ou un alcoxyalkyle contenant au total de 2 à 6 atomes de carbone,

R₂ et R₃, indépendamment l'un de l'autre, ont chacun la signification qui a été donnée pour R₁ ou représentent chacun un radical phényle, benzyle, phényléthyle, cyclopentyle ou cyclohexyle substitué ou non,

R₄ représente un alkyle en C₁-C₄,

R₅ représente un alkyle en C₁-C₄, un cyclopentyle ou un cyclohexyle,

R₆ représente un alkyle en C₁-C₁₂, un phényle, un benzyle, un phényléthyle, un benzoyle, un cyclopentyle, un cyclohexyle, un radical -A₁CN ou un radical -A₁CH₂NH₂,

R₇ représente l'hydrogène ou un radical -A₁CH₂NH₂, ou encore

R₆ et R₇ forment ensemble un radical -(CH₂)_p- dont l'indice p est égal à 4 ou à 5, un radical -(CH₂)₂O(CH₂)₂- ou un radical -(CH₂)₂NH(CH₂)₂-.

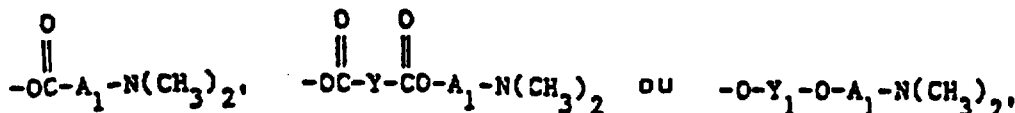
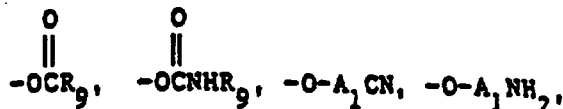


- 43 -

0 145 654

28

ente un radical -OR₉,



R₉ représente un alkyle en C₁-C₁₂, un phényle, un benzyle, un cyclopentyle ou un cyclohexyle,

R₁₀ et R₁₁ représentent chacun, indépendamment l'un de l'autre, un alkyle en C₁-C₄,

R₁₂ représente l'hydrogène, un alkyle en C₁-C₄, un phényle ou un benzyle,

R₁₃ et R₁₄ représentent chacun, indépendamment l'un de l'autre, un atome d'hydrogène ou d'halogène, un alkyle en C₁-C₄, un phényle, un cyclohexyle ou un benzyle,

A et A₁ représentent chacun, indépendamment l'un de l'autre, un radical éthylène, propylène-1,2 ou propylène-1,3,

Y représente la liaison directe, un radical -C_rH_{2r}- dont l'indice r est un nombre de 2 à 10, un phénylène, un toluylène ou un cyclohexylène,

Y₁ représente un radical -C_rH_{2r}- dont l'indice r est un nombre de 2 à 10, un phénylène, un toluylène ou un cyclohexylène,

q représente le nombre 1 ou le nombre 2 et

x représente un nombre de 1 à 3.

3. Procédé selon la revendication 2 dans lequel l'amine est un produit d'addition d'un imidazole de formule VII dans lequel R₁₂ représente l'hydrogène tandis que R₁₃ et R₁₄ ont les significations qui leur ont été données à la revendication 2, avec un éther diglycidyle d'un polyol aromatique, en particulier un éther diglycidyle du bis-(hydroxy-4 phényl)-2,2 propane [bis-phénol A], du bis-(hydroxy-4 cyclohexyl)-2,2 propane [bis-phénol A hydrogéné] ou du bis-(hydroxy-4 phényl)-méthane [bis-phénol F].

4. Procédé selon la revendication 2 dans lequel l'amine est le N,N-diméthyl-N'-(amino-3 propyl) diamino-1,5 propane, le N,N-diméthyl-N'-(cyano-2 éthyl) diamino-1,3 propane, le N,N-diéthyl-N'-benzoyl diamino-1,3 propane ou un mélange de ces composés, ou encore un composé répondant à l'une des formules I, II, VI et VII dans lequel R₁ et R₂ représentent chacun un éthyle ou un méthyle, R₃ représente un phényle non substitué ou un benzyle non substitué, m représente le nombre 2 ou le nombre 3, R₄ et R₅ représentent chacun, indépendamment l'un de l'autre, un méthyle ou un éthyle, q est égal à 1, R₁₀ et R₁₁ représentent chacun un éthyle ou chacun un méthyle, R₁₂ et R₁₄ représentent chacun l'hydrogène, R₁₃ représente l'hydrogène ou un alkyle en C₁-C₄ et x a la signification qui lui a été donnée à la revendication 2.

5. Procédé selon la revendication 2 dans lequel l'amine est un produit d'addition de l'imidazole et d'un éther diglycidyle du bis-phénol F, du bis-phénol A hydrogéné ou du bis-phénol A.

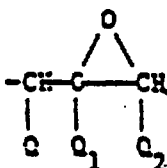
6. Procédé selon la revendication 1 dans lequel le polyol du durcisseur (a) est le résorcinol, l'hydroquinone, le bis-phénol F, le bis-phénol A, le bis-(hydroxy-4 dibromo-3,5 phényl)-2,2 propane, le tétrakis-(hydroxy-4 phényl)-1,1,2,2 éthane, le dihydroxy-4,4' biphenyle, la bis-(hydroxy-4 phényl)-sulfone ou une novolaque dérivant, d'une part, du formaldéhyde ou de l'acétaldéhyde et, d'autre part, du phénol, d'un chlorophénol ou d'un alkylphénol dont l'alkyle contient au plus 9 atomes de carbone.

7. Procédé selon l'une quelconque des revendications 1 à 5 dans lequel le polyol du durcisseur (a) est une novolaque dérivant du phénol, le résorcinol, le bis-phénol F ou le bis-phénol A.

8. Procédé selon la revendication 1 dans lequel la composante durcisseur (a) est un sel du résorcinol, du bis-phénol F ou du bis-phénol A et du tris-(diméthylaminométhyl)-phénol, du diméthylaminométhyl-phénol, du n-propyl-2 imidazole, de la (N,N-diméthylamino-propyl)-amine, de la (N,N-diéthylamino-propyl)-amine ou du N,N-diéthyl-N'-benzoyl diamino-1,3 propane, ou un sel du résorcinol, du bis-phénol F ou du bis-phénol A et d'un produit d'addition de l'imidazole et d'un éther diglycidyle du bis-phénol A ou du bis-phénol F.

9. Procédé selon la revendication 1 caractérisé en ce qu'on utilise, comme durcisseur (a), des sels dans lesquels il y a de 1 à 2 équivalents d'OH par équivalent d'azote.

10. Procédé selon la revendication 1 caractérisé en ce qu'on utilise, comme composante (b), des résines époxydiques qui contiennent en moyenne plus d'un radical répondant à la formule VIII:



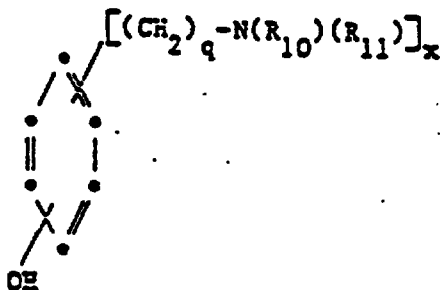
(VIII)-



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- et Q₂ représentent chacun un atome d'hydrogène et Q₁ est un atome d'hydrogène ou un atome de carbone, ou Q et Q₂ forment ensemble un radical -CH₂CH₂- ou -CH₂CH₂CH₂- et Q₁ représente un atome de carbone, fixé à un hétéroatome.
- Procédé selon la revendication 1 caractérisé en ce qu'on utilise, comme composante (b), des éthers diglycidyliques, éventuellement pré-allongés, du bis-(hydroxy-4 phényl)-2,2 propane, du bis-(dibromo-3,5 dihydroxy-4 phényl)-2,2 propane [tétrabromo-bis-phénol A], du bis-(hydroxy-4 phényl)-méthane, du bis-(hydroxy-4 cyclohexyl)-méthane ou du bis-(hydroxy-4 cyclohexyl)-2,2 propane, des éthers polyglycidyliques de novolaques, ou le diamino-4,4' diphénylméthane tétraglycidylé.
12. Procédé selon la revendication 1 caractérisé en ce qu'on utilise, comme composante (b), des éthers diglycidyliques, éventuellement pré-allongés, du bis-phénol A, du tétrabromo-bis-phénol A ou du bis-phénol F, le diamino-4,4' diphénylméthane tétraglycidylé, des éthers polyglycidyliques de novolaques phénol/formaldéhyde ou crésol/formaldéhyde, ou des mélanges de ces composés.
13. Procédé selon la revendication 1 caractérisé en ce qu'on utilise, comme composante supplémentaire (c), des diluants réactifs avec la composante (b).
14. Variante du procédé selon la revendication 1 dans laquelle on utilise, comme durcisseurs (a), des mélanges de diols aromatiques et de sels dérivant de composés répondant à la formule VI:



(VI),

dans laquelle q représente le nombre 1 ou le nombre 2, x un nombre de 1 à 3 et R₁₀ et R₁₁ représentent chacun, indépendamment l'un de l'autre, un alkyle en C₁-C₄, et d'acides monocarboxyliques aliphatiques, saturés ou insaturés et éventuellement ramifiés.

15. Procédé selon la revendication 14 dans lequel on utilise un mélange constitué de bis-phénol A ou de bis-phénol F et d'éthyl-2 hexanoate ou d'oléate du diméthylaminométhyl-phénol ou de tris-(éthyl-2 hexanoate) du tris-(diméthylaminométhyl)-phénol.

16. Procédé selon l'une des revendications 1 et 14, caractérisé en ce que la composante durcisseur (a) est mise en jeu en une quantité telle qu'il y ait de 0,02 à 0,30 équivalent d'azote, plus particulièrement de 0,04 à 0,20, par équivalent d'époxy de la composante (b).

17. Procédé selon l'une des revendications 1 et 14, dans lequel la viscosité du liant à 25°C ne dépasse pas 6 000 mPa.s, plus particulièrement 3 000 mPa.s.

18. Sels dérivant du résorcinol ou du bisphénol A et du diméthylaminométhyl-phénol, du tris-(diméthylaminoéthyl)-phénol ou du n-propyl-2 imidazole, sels dérivant d'une novolaque phénolique et de l'imidazole, du n-propyl-2 imidazole ou d'un produit d'addition de l'imidazole avec un éther diglycidylique du bis-phénol A, et sels dérivant du résorcinol ou du bis-phénol A et d'un produit d'addition de l'imidazole avec un éther diglycidylique du bis-phénol A.