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F. E. BERNETT

3,209,500

CONSTRUCTION MATERIAL

Filed Nov. 13, 1961

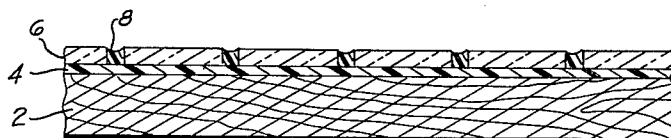


FIG-1

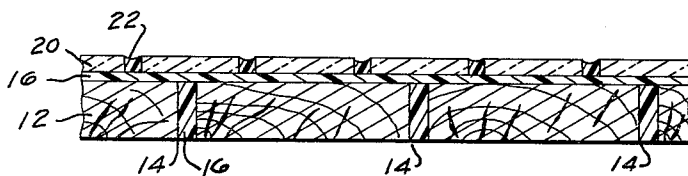


FIG-2

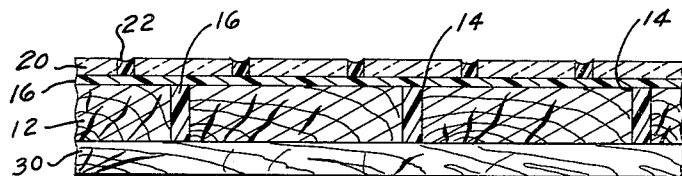


FIG-2a

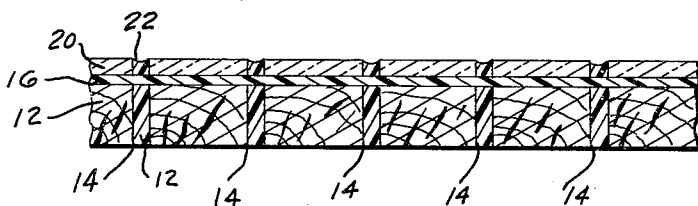


FIG-3

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3,209,500

CONSTRUCTION MATERIAL

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13 Claims. (Cl. 52-309)

The present invention relates to new and useful construction materials, and more particularly to improved construction material comprising a wooden base covered with tile which has unusual strength and wear resistant properties, and which is highly attractive in appearance.

In low cost housing and other buildings, such as industrial buildings, it is conventional and in fact necessary to employ low grade wood and cheap synthetic wood products, such as plywood, chip wood, Masonite, Celotex, and the like, for walling, flooring and other purposes. Low grade wood and cheap synthetic wood products, however, are usually not very attractive. More importantly, such materials usually have poor strength and wear resistance properties, and thus are not able to withstand severe, high impact industrial type service, or even the heavy duty wear of an ordinary household bathroom floor. Such materials are, however, quite economical, and if they could be adapted to withstand severe service and to be attractive, they would offer many advantages over more expensive construction materials.

One possible way of strengthening low grade wood and synthetic wood products is to cover them with ceramic tile.

Heretofore, however, there has been no method available for applying tile, such as ceramic tile, and the like, to wood or wooden products so as to render the resulting construction suitable to withstand severe, high impact, industrial type service.

A difficulty with such a construction in the past has been discovered to be attributable to the type of mortars and grouts employed to bond the tile to the tile, and the tile to the wood or synthetic wood product sub-surface.

The grouts and mortars previously available included cement compositions and the so-called "organic adhesives."

Cement compositions comprise hydraulic cement, such as Portland cement, sand, and other additives to improve bond strength, setting characteristics, and the like. Such compositions are hard and brittle and cannot endure the strain of movement and impact, concomitant, for example, with heavy use of floors.

The so-called "organic adhesives" are solvent systems with rubber or resin binders and inert fillers. One of the leading products of this type on the market today is sold under the trade name "CTA-12," by Minnesota Mining and Manufacturing Company.

The "organic adhesives" are slow to develop strength, are not strong in bond when dried, shrink excessively, and have poor water resistance. They are designed to maintain a large degree of flexibility to offset their inherently low bond strengths. Their flexibility is so great, however, that when used to set tile on wooden substrata, no structural advantage is gained from the layer of tile because stress cannot be transmitted through the adhesive layer. The flexible, weak "organic adhesives" do not support the tile well enough to prevent cracking and chipping of tile under heavy use. Field and laboratory observation have proven the very poor performance of tile installations of this kind on wood when impact loads are prevalent, such as rolling loads on small or hard wheels and women's high heels of small bearing area. All of these disadvantages render such material unsuitable for the type of construction being discussed.

Another difficulty of equal or more serious consequence has been the problem of maintaining proper joints in a

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tile or a similar surface over wood at the joints between wood pieces. Movement between separate wood pieces from thermal or moisture expansion and contraction or from building movement induce concentrated stresses in the tile or similar material layer at the wood joint locations causing damage to the tile or similar material. The only method to prevent this happening, in the past, has been to use expansion joints over the wood joints. Expansion joints are unsightly, however, and pose many difficulties if they are to function properly. In the past, even the most perfect method of bonding tile to wood was susceptible to failure when extended from one piece of wood to another without expansion joints or similar means.

It is an object of the present invention to provide methods for installing ceramic tile on wood or wood products in such a manner as to provide a tile surface more durable than has heretofore been considered possible over wood or wood products.

Another object of the present invention is to provide methods for installing ceramic tile on wood or wood products which increases the load bearing capacity of the wood by significant factors and which produces new and improved floor installations, having unexpectedly high wear resistance properties.

Still another object of the present invention is to provide methods for installing ceramic tiles on wood or wood products with thin bed adhesive layers which are both strong and flexible, and which contain 100 percent solids at the time of application and thereafter.

A further object of the present invention is to provide a method of installing ceramic tile on wood or wood product substrata while simultaneously cementing individual pieces of the substrata together to prevent movement at joints between the pieces of the wood substrata, and to eliminate the need for expansion joints in the tile layer.

Still a further object of the present invention is to provide methods for installing impermeable components to wood or wood products in order to provide a tough continuous vapor barrier over the wood surfaces.

An additional object of the present invention is to provide methods for installing ceramic tile or similar material to wood or wood products, including chipboard, Masonite and Celotex type board to form a protective skin and vapor barrier over the wood substrata, and in order to add significantly to the strength of the board, and to enhance its beauty and durability.

Still another object of the present invention is to provide new methods for the installation of ceramic tile or similar material to wood and wood products which is particularly suitable for floor surfaces.

Still another object of the present invention is the provision of new and improved construction materials which comprise a wood or wood product substrata having superimposed thereon and bonded thereto ceramic tile, the resulting construction material having improved properties of strength and durability.

Another object of the present invention is to provide a method of installing ceramic tile on counter tops directly on wood surfaces which will impart higher impact strength to the tile than has heretofore been possible so that dropping of heavy objects such as pots and crockery on the counter top will not crack and chip the tile, thereby avoiding unsightly and unsanitary conditions.

Another object of the present invention is to provide an improved method of applying ceramic tile to wood panels which enhances the panels structurally and decoratively, and more particularly, improve their impact resistance, moisture sensitivity and flexural strength. The resulting panels are suitable for use as curtain walls, wall

surfacing board, counter tops and the like, where wood alone is wholly or partly objectionable.

Another object of this invention is to provide a method for installing ceramic tile so that the finished installation will have the durability, under heavy service, of conventional all-masonry installations without the high degree of resilience of all-masonry installations which are reported to be tiring and harmful to the legs of people standing and walking on them for long periods of time.

The methods and construction materials disclosed herein are especially suitable for use in flooring. Flooring produced according to the teachings contained herein is far superior to wooden flooring alone. The new and novel constructions and methods incorporate a grouted joint between the tile and other components which is strong, flexible and resilient; able to absorb impact without causing damage to the tiles; able to absorb bending of the surface without causing damage to the tiles.

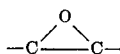
According to the present invention, it has been discovered that new and useful flooring constructions can be made by bonding ceramic tiles to wooden substrata with epoxy resin, which upon curing, has certain characteristics.

The characteristics of the cured epoxy resin suitable for use in the present invention are as follows: (1) virtually no shrinkage; (2) a relatively high compressive strength, which is at least, or in excess of 3000 p.s.i.; (3) an elastic modulus of at least 0.05×10^6 , and preferably at least 0.5×10^6 ; (4) a tensile strength at least $\frac{1}{2}$ of the compressive strength; and (5) a bond strength to ceramic tile and wood in excess of 400 p.s.i., measured in shear.

All of these properties of the cured epoxy resin in the order of magnitudes indicated are necessary for good performance of the installation, particularly to prevent tile breakage under high load; to prevent chipped tile edges and grout; to prevent cracks between tile and grout; and to prevent loss of bond between tile and wood which is essential to obtain increased strength of the assembly over that of wood alone.

The epoxy resins suitable for use in the present invention and having the properties disclosed hereinabove are preferably 100 percent solid systems, and may either be a multipart system, with epoxy resin and hardener stored separately, or a one part system, with epoxy resin and hardener in intimate admixture, and capable of being activated by addition of suitable, readily available polar liquids, such as water, alcohol, and the like.

The resinous epoxides suitable for use in the present invention comprise those compounds having the reactive epoxy resin group



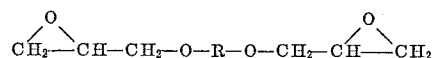
The polyepoxides may be saturated or unsaturated, aliphatic, cycloaliphatic, or heterocyclic and may be substituted if desired with substituents such as chlorine atoms, hydroxyl groups, ether radicals and the like. They may also be monomeric or polymeric.

Examples of the polyepoxides include, among others, epoxidized glycerol dioleate, 1,4-bis(2,3-epoxypropoxy) benzene, 1,3-bis(2,3-epoxypropoxy) benzene, 4,4'-bis(2,3-epoxypropoxy) diphenyl ether, 1,8-bis(2,3-epoxypropoxy)-octane, 1,4-bis(2,3-epoxypropoxy) - cyclohexane, 4,4'-bis(2-hydroxy - 3,4'-epoxybutoxy) - diphenyldimethylmethane, 1,3-bis(4,5 - epoxybutoxy) -5-chlorobenzene, 1,4-bis(3,4-epoxybutoxy)-2-chlorocyclohexane, 1,3-

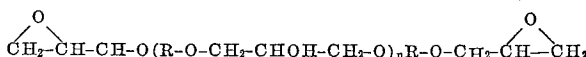
bis(2-hydroxy-3,4-epoxybutoxy) benzene, 1,4-bis and (2-hydroxy-4,5-epoxypentoxy) benzene.

Among the preferred epoxides are the epoxy polyethers of polyhydric phenols obtained by reacting a polyhydric phenol with a halogen containing epoxide or dihalohydrin in the presence of an alkaline medium. Polyhydric phenols that can be used for this purpose include, among others, resorcinol, catechol, hydroquinone, methyl resorcinol, or polynuclear phenols, such as 2,2-bis(4-hydroxyphenyl) propane (Bis-phenol A), 2,2-bis(4-hydroxyphenyl) butane, 4,4'-dihydroxybenzophenone, bis(b-hydroxyphenyl) ethane, 2,2-bis(4-hydroxyphenyl) pentane, and 1,5-dihydroxynaphthalene. The halogen-containing epoxides may be further exemplified by 3-chloro-1, 2-epoxybutane, 3-bromo-1, 2-epoxyhexane, 3-chloro-1,2-epoxyoctane, and the like.

The monomer products produced by this method from dihydric phenols and epichlorohydrin may be represented by the general formula:



wherein R represents a divalent hydrocarbon radical of the dihydric phenol. The polymeric products will generally not be a single simple molecule but will be a complex mixture of glycidyl polyethers of the general formula:

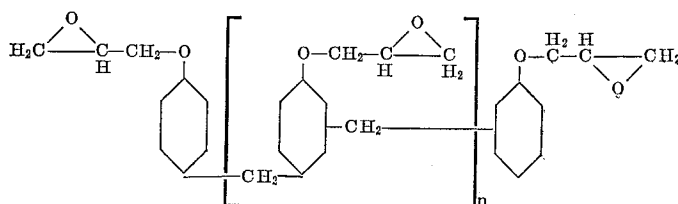


30 wherein R is a divalent hydrocarbon radical of the
dihydric phenol and n is an integer of the series 0, 1, 2,
3, etc. While for any single molecule of the polyether n
is an integer, the fact that the obtained polyether is a mixture
35 of compounds causes the determined value for n to
be an average which is not necessarily zero or a whole
number. The polyethers may in some cases contain a
very small amount of material with one or both of the
terminal glycidyl radicals in hydrated form.

The aforementioned glycidyl polyethers of the dihydric phenols may be prepared by reacting the required proportions of the dihydric phenol and the epichlorohydrin in an alkaline medium. The desired alkalinity is obtained by adding basic substances, such as sodium or potassium hydroxide, preferably in stoichiometric excess to the epichlorohydrin. The reaction is preferably accomplished at temperatures within the range of from 50° C. to 150° C. The heating is continued for several hours to effect the reaction and the product is then washed free of salt and base.

These epoxide resins are available in several forms varying from a viscous liquid to a solid resin. Especially suitable are those resins which are liquid or near their softening point at room temperature.

55 Typical of the epoxy resins which may be employed are the epichlorohydrin-bis-phenol type sold under the trademarks "Epon Resins" (Shell Chemical Corporation), "Gen Epoxy" (General Mills), "DER Resins" (Ciba), "ERL Resins" (Bakelite Corporation), "Epi-Rez" (John
60 Dabney); the paracetic acid-epoxidized compounds sold under the trademark "Unox Diepoxides" (Union Carbide Chemical Company); and the trifunctional epoxy compounds sold under the trademark "Epiphen" (The Borden Company). An example of the trifunctional type of
65 compounds is "Epiphen" ER-823, which has the following formula:



where n is a number such that from about 180 to 200 grams of the resin contain about one gram mole of epoxide group.

The epoxide resins suitable for use in the present invention may contain between about 5 and 400 percent, and preferably between about 10 and 300 percent, by weight, based on the weight of epoxy resin, of an inert, finely divided solid.

Suitable finely divided inert solid materials for use with the epoxy resins include fillers, such as asbestos, albality, silica, mica, flint powder, quartz, kryolite, Portland cement, limestone, atomized alumina, barytes, talc, pyrophyllite, various clays, diatomaceous earth, and other like materials. Also may be mentioned pigments, such as titanium dioxide, cadmium red, carbon black, aluminum powder, and the like.

Suitable other colorants may be added to the epoxy resin if desired. Typical of these are: National Fast Red (National Aniline); Calco Condensation Green A.Y. (American Cyanamid); Calco Condensation Blue (American Cyanamid); Bismark Brown (National Aniline); Blue Lake (13% Ponsal Blue, 10% aluminum hydrate and 77% blanc fixe), Krebs BP-179-D, Blue Lake Krebs BP-258-D, Lithol Tower, Chrome Yellow, Iron Blue, Milari Blue, Monastral Green, Maroon Toner, Chrome Green, Chrome Orange, Iron Oxide Reds, Aluminum Powder, and flattening agents like diatomaceous silica and silica aerogel. The color materials should be selected, however, so as to be non-reactive with the epoxy resins and other ingredients at atmospheric temperature, as otherwise this might cause poor storage stability and also affect the retention of adhesiveness.

The finely divided inert solid materials suitable for use herein may have an average particle size ranging between about 50 mesh and 400 mesh, and preferably between about 100 and 400 mesh (U.S. Std. Series). The exact size of the inert finely divided solid materials will depend upon the particular application of the compositions.

In addition to finely divided solid materials, a wide variety of resinous modifiers may be added to the epoxy resin systems disclosed herein. Among these may be mentioned the phenolic resins, such as aniline formaldehyde resins; urea resins, such as urea formaldehyde resins; melamine resins, such as melamine formaldehyde resins; polyester resins, such as those produced from polybasic acids and polyhydroxyl alcohols and which may contain free carboxyl groups and/or aliphatic hydroxyls capable of reacting with the epoxy resins; vinyl resins such as vinyl chloride, vinylidene chloride and the like; and polystyrene. The addition of such resinous modifiers is well understood in the art. The resinous modifiers may vary from about 1 to about 100 percent or more, by weight, based on the weight of the epoxy resin.

An especially suitable resinous modifier for use in the present invention is polystyrene resin, and this resinous modifier is preferred. The polystyrene resin should vary from about 10 to about 50 percent, and preferably from about 20 to 40 percent, by weight, based on the weight of the epoxy resin. Polystyrene resin, it has been discovered, considerably enhances the flexibility of the bonds produced with the epoxy resin compositions disclosed herein.

The epoxy resins may also have incorporated therein, if desired, a lubricant, such as silicone oils, silicone jelly, petroleum jellies, and so forth. As an example of the silicone oil may be mentioned organo-siloxane liquid supplied by General Electric Company as Silicone Liquid No. 81069. Any of the commercially available silicone jellies which are sold under a wide variety of trademarks and trade names may be used.

Typical of the curing or cross-linking agents for epoxy resins may be mentioned the amine curing agents, i.e., amines containing at least 1 and preferably at least 2

amino nitrogen atoms, e.g., polyamines. Such materials include ethylene amine, ethylene diamine, propylene diamine, diethylene triamine, dipropylene triamine, triethylene tetramine, tripropylene tetramine, tetraethylene pentamine, tetrapropylene pentamine, and mixtures of the foregoing. Also may be mentioned higher alkyl polyamines, such as alkyl polyamines in which the alkyl group is butyl, hexyl, octyl, and so forth.

Due to their greater availability, commercially produced polyfunctional amines may also be used as hardeners. Examples of such commercially available amines are those obtained from the Chemical Division of Armour & Company under the trade names "Duomeen O" and "Duomeen S." "Duomeen O" consists essentially of a mixture of N' alkyl trimethylene diamines derived from technical grade oleic acid. The alkyl group content is distributed as follows:

	Percent
C_{14} -----	2
C_{16} -----	5
C_{18} -----	93

"Duomeen S" consists essentially of a mixture of N -alkyl trimethylene diamines derived from soya acids. The alkyl group content is distributed approximately as follows:

	Percent
C_{16} -----	13
C_{18} -----	87

Preferred curing or cross-linking agents for the epoxy resin compositions used in the present invention may be described as poly-amido-amine epoxide hardeners. Epoxy resins cured with such hardeners, it has been discovered, have the unique and unexpected property of being water soluble. Additionally, and very importantly, epoxy resins cured with such hardeners have the physical properties described hereinabove and are therefore suitable for use in the construction materials of the present invention.

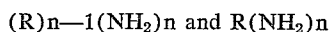
The poly-amido-amine epoxide hardeners are produced by copolymerization of polyamines with polycarboxylic acids, the copolymerization reaction being permitted to proceed to such an extent that the products produced are soluble in both epoxy resin and water.

In conducting the copolymerization reaction, it is important that excess polyamine be used, so that unreacted polyamine is present in the resulting copolymer. In the case where no unreacted amine remains, water solubility is lost and the products do not possess the required ability to harden an epoxide polymer. Nor are such reaction products soluble in the epoxy resin and water.

Suitable amine hardeners are prepared by reacting the polyamines and polycarboxylic acids described herein at temperatures below the decomposition temperature of the polyamines by employing the appropriate polyamine in stoichiometric excess of that theoretically required to react with the appropriate polycarboxylic acid. The temperature of the reaction is preferably between about 100° and 200° C. Especially good results are achieved when the temperature is between about 120° and 160° C.

Aliphatic polyamines containing two or more amino nitrogens may be used to produce such poly-amido-amine hardeners. Polyamines containing primary nitrogens are especially suitable.

Polyamines suitable for making the poly-amido-amine compounds disclosed herein have the formulae:



where R is a hydrocarbon radical and n is an integer having a value of at least 2, and preferably between about 4 and 10. Such polyamines should have a formula weight of at least 60 and preferably between about 90 and 500.

Examples of polyamines that may be used to produce such hardeners include ethylene diamine, propylene di-

amine, diethylene triamine, dipropylene triamine, triethylene tetramine, tripropylene tetramine, tetraethylene pentamine, tetrapropylene pentamine, and mixtures of the foregoing. Also may be mentioned higher alkyl polyamines satisfying the above formulae, such as alkyl polyamines in which the alkyl group is butyl, hexyl, octyl and so forth. The hydrocarbon radical R_1 attached to the amino nitrogen atoms may have up to 50 carbon atoms or more. Preferably, however, the hydrocarbon radical has fewer than about 30 carbon atoms.

Especially suitable are polyamines which have a value of n of at least 4, or polyamines wherein the formula weight of R is greater than about 90. It has been found that where polyamines are used in which n is an integer less than 4, or R is of a molecular weight lower than 90, satisfactory hardening action is not obtained. This is believed to be due in part to the reaction of such low molecular weight polyamines with polycarboxylic acids to form compounds having a high melting point, which compounds require high reaction temperatures, e.g., above the decomposition temperature of the polyamines, to effect the fusion which precedes the amidation reaction. The same problems are experienced when, for example, a polycarboxylic acid, e.g., $R(COOH)_2$, is employed wherein R is of low molecular weight. A further difficulty found to exist when low molecular weight polyamines and polycarboxylic acids are used is that the reaction products produced are insoluble in epoxide polymers and therefore are not able to function as hardeners.

The polycarboxylic acids suitable for reaction with the above described polyamines to produce poly-amido-amine epoxide hardeners have at least two carboxyl groups and may be represented by the formula $R(COOH)_n$, where R is a hydrocarbon radical which may be saturated or unsaturated, aliphatic, cyclicaliphatic, or heterocyclic, and n is an integer having a value of at least 2. Among the preferred polycarboxylic acids are the straight chained saturated dicarboxylic acids such as adipic, pimelic, suberic, azeloic, sebacic, nonone dicarboxylic acid, and the higher members of this series, including mixtures thereof. Also may be mentioned the straight chained unsaturated dicarboxylic acids, including citraconic acid, mesaconic acid and itaconic acid. Especially suitable for use are the so-called resin acids. These may be classified as diterpene acids, a major constituent being abietic acid. When such diterpene acids are dimerized, a dicarboxylic acid results. Particularly useful are those diterpene acids which, upon being dimerized, have a formula weight of about 300 to 900, and preferably between about 500 to 600.

The poly-amido-amine epoxide hardeners are produced by dissolving the polycarboxylic acid and polyamine in a suitable organic solvent, in which the polyamine and the polycarboxylic acid are soluble. The amount of the polyamine is in excess of that stoichiometrically required to react with the polycarboxylic acid. The amount of excess polyamine is preferably at least about 5 percent, and may be between about 5 and 200 percent, or higher, and preferably between about 50 and 150 percent, based on the polycarboxylic acid. The solvent employed is not critical, since after mixing the solvent is preferably removed, for example, by evaporation. The residue remaining after solvent evaporation is then heated to a temperature of between about 100 to 200° C., care being taken that the temperature employed is below the decomposition temperature of the polyamine used. The time of heating should be at least about one-half hour, or between about 1 and 25 hours, and is preferably between about 1 and 16 hours. Although the solvent is preferably removed prior to heating, it should be understood that the solvent may also be removed after heating.

When liquid epoxide resin compositions are used, the adhesive compositions may be produced by simply dissolving the hardener in the liquid epoxide resin. When the epoxide resin is solid, the epoxide resin may be dissolved in a suitable solvent prior to the addition of the

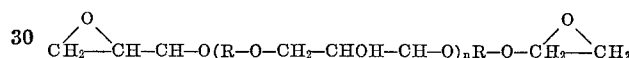
hardening agents. Suitable solvents which dissolve the epoxide resins include phenyl glycidyl ether, acetone, methyl ethyl ketone, isophorone ethyl acetate, butyl acetate, ether alcohols such as methyl, ethyl or butyl ether of ethylene glycol, and so forth.

Specific examples embodying epoxy resin systems cured by the poly-amido-amine agents disclosed hereinabove and preferred for use in making the improved construction materials of the present invention are as follows:

EXAMPLE 1

The prime poly-amido-amine hardener was prepared by dissolving 14.6 parts by weight of adipic acid in 100 parts by weight of ethyl alcohol and to this mixture were added 40.0 weight parts of N-octadecene trimethylene diamine. After solution was effected, the resulting mixture was heated to evaporate the alcohol, then placed for 16 hours in an oven held at 120° C. Upon cooling an orange-brown paste was obtained. This was slowly soluble in an equal weight of water yielding a gelatinous solution.

The epoxide polymer used was of the epichlorohydrin-bisphenol of acetone type, having a viscosity of about 13,000 centipoises (25° C.), an epoxide equivalent of approximately 200, and a melting point in the range of 8 to 12° C. The epoxide polymer was a complex mixture of glycidyl polyether and had the following general formula:



The orange-brown paste produced was added to an equal weight of the liquid epoxide polymer described hereinabove. An adhesive composition which hardened on standing was obtained.

The adhesive composition was effectively and readily hardened in the presence of water, and was capable of being readily removed from surfaces upon application of a water-soaked cloth.

EXAMPLE 2

As a comparison for Example 1, an adhesive composition was prepared by dissolving N-octadecene trimethylene diamine in an equal weight of the liquid epoxy resin polymer described in Example 1. The resulting composition did not readily or effectively harden in the presence of water and aqueous alkali and acid solutions. Nor was it removable from a surface by application of a water-soaked cloth.

EXAMPLE 3

As a comparison for Example 1, and following the procedure of Example 1, stoichiometric amounts of dimerized tall oil resin were reacted with the following amines by heating at 155° C. for 1 hour:

Ethylene diamine
Diethylene triamine
Tetraethylene pentamine
N-alkyl (C_{14-18}) trimethylene diamine

The products of these reactions were added to an equal weight of the liquid epoxide resin described in Example 1. The resulting adhesive compositions did not effectively harden, and did not exhibit the water-cleanability characteristic of the adhesive compositions of Example 1.

EXAMPLE 4

Example 3 was repeated, except that in preparing the amine hardener, the amines were added to the dimerized tall oil resins in an amount which was 100 percent in excess of that stoichiometrically required to react with the dimerized tall oil.

When added to the liquid epoxide resin of Example 1, water-cleanable compositions were obtained which readily and effectively hardened.

EXAMPLE 5

The procedure of Example 1 was followed, but with substitution of an epoxide resin of the epichlorohydrin-bisphenol of acetone type having an epoxide equivalent of about 185 and a viscosity of approximately 7,000 centipoises (25° C.). The resulting composition was more fluid than that obtained in Example 1, and again showed the same water-cleanability characteristics, and good hardening characteristics of the composition produced in Example 1.

EXAMPLE 6

The procedure of Example 1 was followed but with substitution of a solid epoxide polymer of the epichlorohydrin-bisphenol of acetone type. The solid epoxide resin was dissolved in phenyl glycidyl ether, at a 4:1 resin:ether ratio. The epoxide polymer had a melting point of about 42° C. and an epoxide equivalent weight of 500. The resulting composition had properties similar to those obtained in Example 1.

EXAMPLE 7

10 weight parts of sebacic acid were dissolved in 385 parts of ethyl alcohol and to this were added 17.8 weight parts of "Duomeen S," a product of the Armour Company. The "Duomeen S" consisted of a mixture of N-alkyl trimethylene diamines derived from technical grade soya acids. The alkyl group content was distributed as follows:

	Percent
C ₁₄ -----	2
C ₁₆ -----	5
C ₁₈ -----	93

This solution was then heated to evaporate the alcohol and then heated at 155° C. for 2 hours. The soft resinous product obtained was dissolved in an equal weight of liquid epoxide polymer of the type described in Example 1, and the resulting composition exhibited the same water-cleanability and good-hardening characteristics as the adhesive composition produced in Example 1.

EXAMPLE 8

A resin base and pigment hardening composition were prepared using the following formulae:

The resin base:

28.9 weight parts epoxide resin
14.3 weight parts titanium dioxide pigment
11.4 weight parts polystyrene resin
45.4 weight parts blanc fixe

Pigment-hardener composition:

28.0 weight parts amido-amino tall oil resin
1.7 weight parts diethylene triamine
68.5 weight parts blanc fixe
1.8 weight parts silica aerogel

The epoxide resin used was of the epichlorohydrin-bisphenol of acetone type described in Example 1. The amido-amino tall oil resin was that produced in Example 4 by the reaction of dimerized tall oil with excess tetraethylene pentamine at a temperature of 155° C.

The resin base and pigment-hardener composition were mixed, and a smooth, white, easily spreadable composition was produced.

EXAMPLE 9

The following resin-base was prepared:

63.5 weight parts of epoxide resin
5.5 weight parts of phenyl glycidyl ether
1.3 weight parts (2,2' bis(-hydroxyphenyl)propane)
26.7 weight parts of polystyrene resin
3.0 weight parts of petroleum jelly

and mixed with 3.33 times its weight of the following filler-hardener composition:

11.2 weight parts amido-amino tall oil resin, equivalent weight of 135, viscosity at 25° C. of 250 centipoises
0.25 weight parts diethylene triamine
85.6 weight parts sand (through 30 mesh screen)
2.8 weight parts silica aerogel
.05 weight parts carbon black

The epoxide resin was of the solid type described in Example 6. It had an epoxide equivalent of about 500, a viscosity of approximately 7,000 centipoises (25° C.), and a melting point of about 42° C.

The poly-amido-amino tall oil resin was produced according to the procedure of Example 4 by reacting dimerized tall oil resin with 100 percent excess tetraethylene pentamine (based upon the stoichiometric amount of a tall oil resin), at a temperature of 155° C.

This gave a trowellable composition that was used to set ceramic quarry tiles on a wooden substrata and to subsequently fill the joints between these. Excess material was removed from the tile face by mopping with a sponge wet with water. Hard, adherent, chemically resistant bonds and joints were obtained.

The epoxy resin systems of Examples 8 and 9 may be improved, if desired, by addition of a small amount of water to the filled epoxy resin component, i.e., the epoxy resin plus fillers and pigments, prior to the addition of the hardening agent. The addition of water produces a gel-like structure in the composition which is extremely stable on storage, and, when the resulting epoxy resin is hardened, an epoxy resin adhesive is produced which has improved flow and sag properties, when compared to similar compositions to which water has not been added. The amount of water added may vary from about 0.5 to 15 percent, based upon the weight of epoxide resin.

The following example illustrates an epoxy resin adhesive system to which water has been added to the filled epoxy resin portion to gel the epoxy resin prior to addition of the hardening agent.

EXAMPLE 10

The prime poly-amido-amine hardener was prepared by dissolving 14.6 parts by weight of adipic acid in 100 parts by weight of ethyl alcohol and to this mixture were added 40.0 weight parts of N-octadecene trimethylene diamine. After solution was effected, the resulting mixture was heated to evaporate the alcohol, then placed for 16 hours in an oven held at 120° C. Upon cooling an orange-brown paste was obtained. This was slowly soluble in an equal weight of water yielding a gelatinous solution.

A resin base and pigment-hardener composition were prepared.

The resin base had the following composition:

	Percent by weight
Epoxide resin (Epon 820) -----	29.86
Polystyrene resin -----	8.89
Titanium dioxide -----	19.27
Blanc fixe -----	39.04
Water -----	2.40
	100.00

The pigment-hardener composition had the following composition:

	Percent by weight
Poly-amido-amine hardener -----	31.90
TiO ₂ -----	8.62
Blanc fixe -----	45.69
Silica (325 mesh) -----	13.79
	100.00

The epoxide resin used was the same as that described in Example 6. The poly-amido-amine epoxide hardener was that prepared in this example, supra.

1.5 parts by weight of the resin base were mixed with 1.0 parts by weight of the pigment-hardener composition, and a smooth, easily spreadable composition was produced. The composition was spread over a wooden surface and glazed ceramic tiles in spaced relation laid thereon. The joints between the tiles were filled by spreading more of the composition over the tiles, thus filling the joints. Excess material was removed from the face of the tiles by scraping with a trowel edge and then wiped clean with a water-soaked cotton cloth. Hard, impermeable bonds and joints were thus obtained. The composition exhibited extremely good flow resistance and non-sagging properties in the joints.

In addition to two-part systems, all powder one-part epoxy systems may also be used to prepare epoxy resin adhesive compositions suitable for use in the present invention.

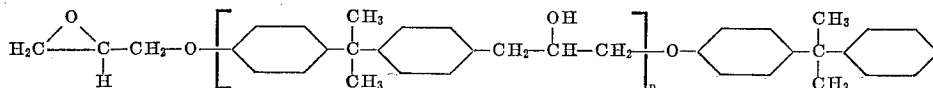
A suitable one-part dry, 100 percent solid epoxy resin system for use in the present invention comprises an epoxy resin of the type described herein, an acid salt of a polyamine and a strong base. At the time of use, a polar liquid, such as water, alcohol, and the like, is added to the dry mix to initiate polymerization.

The mechanism and sequence of events which take place when the liquid is added to the dry composition are believed to be as follows:

Liquid+base+acid salt of polyamine gives:

- (a) Solution of base+solution of acid salt of polyamine;
- (b) Solution of base+solution of acid salt of polyamine gives a free amine+water;
- (c) Free amine+epoxide compound gives epoxide polymer.

In Step (a) the addition of sufficient liquid transforms the dry powdery mixture to a fluid form as well as dissolving the base and the acid salt of the polyamine. The solution of these two products causes them to react according to Step (b) to yield the free amine. Finally the free amine reacts with the epoxide monomer or prepolymer as shown in Step (c) forming the cross-linked



to the mechanism set forth above, but it is believed to be the probable description of the chemical process involved.

The polyamine acid salts may be prepared by reacting suitable polyamines with organic or inorganic acids, such as hydrochloric, sulfuric, nitric, phosphoric, acetic, formic, and the like. The polyamines suitable for use are those indicated above in connection with the poly-amido-amine epoxide hardeners.

Strong bases include the alkali and alkaline earth metal hydroxides, although sodium and potassium hydroxide are preferred.

The use of silica aerogel and finely divided sand in combination as carrier and aggregate for the components of the one-part, all powder epoxy systems under discussion serves two functions. These materials insure the availability of a great surface on which the cross-linking of the epoxide resins and the amine hardeners will take place. The sand moderates the speed of reaction by taking up a considerable amount of the exothermal heat produced by the initial solution of some of the components and the heat produced during the cross-linking of the amine and epoxide resin. When the balance is changed in favor of greater amounts of aerogel the curing rate is increased due to the greater amount of heat available to the reaction but shrinkage of the composition is increased also. A balance between rate of curing

epoxide polymer. We do not wish to restrict ourselves and ultimate shrinkage may be obtained by varying the amounts of filler in the form of aggregate and carrier which are included in the dry compositions.

Liquid epoxide resins and liquid amine hardeners in salt form through adsorption on the aerogel and sand are made substantially dry and can be contacted with each other without initiating any appreciable degree of polymerization. The mixtures are relatively uniform and therefore may be prepared in such manner that any portion may be removed from the whole and still retain substantially the proportion of epoxide resin and amine hardener which were originally determined to be most suitable for the particular ingredients used in making up the dry composition.

Compositions of the type described will, if exposed to unduly great amounts of water, partially react but this quality is not such that it would be proper to characterize the compositions as water-sensitive. Their sensitivity to water in the form of humidity or other vapor lies between Portland cement and calcium chloride. The compositions therefore may be shipped in plastic-lined paper bags and the like without other special precautions being necessary.

Specific examples of one-part, 100 percent solid epoxy resin compositions having the properties described hereinabove are given in the following examples:

EXAMPLE 11

The hydrochloric acid salt of diethylene triamine was prepared by mixing 129 weight parts of 37 percent hydrochloric acid with 45 weight parts of diethylene triamine, dissolved in 200 weight parts of water. The water was evaporated from this solution by drying at 110° C. and a crystalline salt residue obtained.

100 weight parts of a liquid epoxide resin were mixed with 233 parts of a fine, 100 mesh, silica sand and 40 parts of silicon dioxide aerogel. The epoxide resin was of the epichlorohydrin-bisphenol of acetone type, having a viscosity of about 22,000 centipoises, an epoxide equivalent of approximately 200, and a melting point in the range of 8 to 12° C. Its structural formula is represented as:

The silicon dioxide aerogel had a particle size in the range of 0.5 to 3.0 microns and a specific surface area of about 200 square meters/gram. The function of the addition of the sand which may have a particle size between 16 and 300 mesh and silicon dioxide aerogel is that of converting the liquid polymer into the form of free-flowing powder.

The following powder mixture was prepared:

15 weight parts of the acid salt prepared above
373 weight parts of the resin powder prepared above
8.4 weight parts of powdered sodium hydroxide

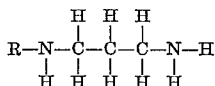
This composition yielded a free-flowing powder, remarkably stable upon long-term storage, even though comprising acidic and basic constituents in intimate contact with one another. When 92 weight parts of water were added to this powder a fluid, coherent mix was obtained. This was troweled onto a wooden floor surface, at a thickness of approximately 3/32" and used (as a setting bed-adhesive) for ceramic tile. After a period of 24 hours the material had hardened and a strong bond developed to the wooden surface and the underside of the tile.

EXAMPLE 12

The hydrochloric acid salt of N-octadecene trimethylene diamine was prepared by reaction of 42 weight parts

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of 37% hydrochloric acid with 84.4 weight parts of the diamine. The N-oleic trimethylene diamine is prepared by the reaction of octadecyl amine, derived from oleic acid, with acrylonitrile and subsequently hydrogenating this product. Its structural formula is represented as follows:



where R indicates a C_{18} alkyl grouping. 15 weight parts of the aerogel described above were then mixed into this salt to produce a free-flowing powder.

In order to produce a more finely divided resin powder 21.4 weight parts of the liquid epoxide resin described in Example 11 were dissolved in an equal weight of ethyl alcohol and into this 8.6 weight parts of aerogel and 70 parts of fine white silica sand were mixed. The alcohol was then evaporated from this slurry, yielding a colorless, free-flowing powder.

The following powder mixture was prepared:

62.3 weight parts of the acid salt
36.3 weight parts of the resin powder
1.4 weight parts of sodium hydroxide

This composition yielded a fine, free-flowing powder, which subsequently required 16.5 percent of its total weight of water to give a fluid composition. This composition was used as a jointing compound, placed between the edges of tile bonded to a wooden floor. Exceptional ease in cleaning excess material from the tile faces was noted and hard, chemically resistant joints were obtained.

EXAMPLE 13

The following composition (based on weight):

	Percent
Hydrochloric acid salt of N-octadecene trimethylene diamine	11.2
Silicon dioxide aerogel	7.7
Fine sand	63.0
Epoxide resin	15.0
Powdered sodium hydroxide	3.1

when mixed with 16.2% of its weight of water gave a fluid composition, suitable for use as a chemically resistant setting bed or jointing compound for ceramic tile on wooden surfaces. This material showed relatively early development of hardness. The epoxide resin referred to in this example was of the polyfunctional type, and contained one gram-mole of epoxide group per 180 to 200 grams of resin.

EXAMPLE 14

The following composition (based on weight):

	Percent
Epoxide resin of Example 11	19.5
Titanium dioxide	8.0
Silicon dioxide aerogel	9.7
Hydrochloric acid salt of N-octadecadiene diamine	18.3
Wollastonite (300 mesh)	40.0
Powdered sodium hydroxide	4.5

when mixed with 28% of its weight of water gave a creamy, non-granular, white, fluid composition suitable for use to set and grout ceramic tile on wooden surfaces.

EXAMPLE 15

The following composition (based on weight):

	Percent
Hydrochloric salt of "Duomeen O"	6.2
Epoxide resin of Example 11	8.4
Silicon dioxide aerogel	4.2
Powdered sodium hydroxide	1.3
Fine sand	79.9

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mixed with 16 percent of its weight by water gave a smooth, viscous paste composition which developed a strong resistant bond between a wood substrata and ceramic tiles which was substantially set at the end of 24 hours.

EXAMPLE 16

The following composition (based on weight):

	Percent
Hydrochloric salt of "Duomeen S"	6.2
Epoxide resin of Example 11	7.5
Silicon dioxide aerogel	3.2
Powdered sodium hydroxide	3.0
Fine sand	80.1

mixed with 15% of its weight by water resulted in an excellent setting and grouting composition for adhering tiles to wooden substrata and showed a minimum of contraction upon hardening.

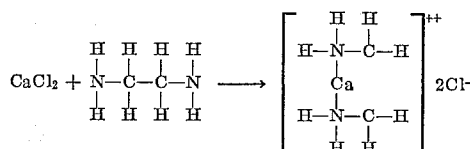
Such further dry, all-powder one-part mixes suitable for use in the present invention comprise an epoxy resin and a complex amine hardener produced by the reaction of a metal salt and a diamine or polyamine. At the time of use, a suitable polar liquid, such as water, alcohol, and so forth, is added to the dry mix to activate the hardener and cure the epoxy resin to produce epoxy resin adhesive compositions having the properties described above, and suitable for use in making the new and novel construction materials disclosed herein.

Suitable di- or poly-amines for making the complex amine salts which serve as hardeners in the one-part epoxy systems under discussion have been described hereinabove in connection with the poly-amido-amine hardeners.

The metal salts suitable for use in preparing the hardeners of the systems under discussion are those capable of releasing cations which form stable complexes with amines. Typical of these are the strong and weak mineral and organic acid salts of calcium, zinc, copper, silver, and nickel. Of these, exceptionally good results are achieved with calcium and zinc salts and these are preferred. The anions of the salts are not critical. For example, the halides, nitrates, sulfates, phosphates, acetates, and other weak and strong mineral and organic acid salts of these metals may be employed, as will be readily apparent to those skilled in the art.

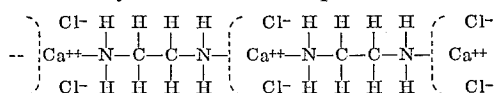
In preparing the hardeners, the metal salts capable of yielding cations which react with amino groups to form stable complexes are added, preferably in finely divided form, to the polyamines described hereinabove, and the mixture is agitated. The time of reaction and temperature will depend upon the particular polyamine and metal salts used. Completion of the reaction is indicated by disappearance of the polyamine and the appearance of powder in those cases where the reaction is conducted below the melting point of the reaction product. When the reaction is conducted above the melting point of the reaction product, the reaction is continued until a homogeneous mixture appears, at which time the reaction product may be cooled to below its melting point to give a solid material which may be pulverized to a powder. In those instances where the complex amine reaction product is a liquid, this may be suitably absorbed on a carrier, as will be explained more fully hereinbelow.

Illustrative of the amine complex compounds which serve as hardeners for the one-part epoxy system now under discussion are those produced when calcium chloride is reacted with ethylene diamine. This reaction may be illustrated as follows:



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More realistically, the reaction product has probably a continuous crystalline structure represented as:



and extending, of course, in three dimensions. As can be seen, the complex hardeners may be described as stable amine complexes of metal salts and polyamines. The structures of other stable amine complexes will readily suggest themselves to one skilled in the art from the foregoing description.

The complex inorganic salt-polyamine hardeners may be mixed with epoxy-type polymers or monomers of the liquid or solid type described hereinabove.

In the epoxy resin systems under discussion, suitable fillers and pigments may be added, as has already been described hereinabove.

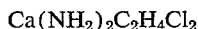
In forming epoxy resin bonding compositions from one-part systems containing the complex inorganic salt-polyamine hardening agents, enough of the hardeners are added to the epoxy resin composition to insure that upon activation, good hardening is achieved. Preferably the hardeners and epoxy-resin prepolymers are present in the dry compositions in stoichiometric proportions. Depending on the nature of the adhesive composition desired, however, greater or lesser amounts of the hardener may, of course, be used.

When water or other polar solvents are added to the compositions to make them functional, i.e., to initiate and cause polymerization, it is believed that a hydrate, alcoholate or other similar complexes of the metal salt portion of the amine hardener are formed, thereby displacing the free amine, which is then available for reaction and hardening of the epoxide resin. Although not wishing to be restricted to the description set forth above, it is believed to be the probable description of the chemical process involved.

Specific examples of all-powder, one-part epoxy systems containing the complex inorganic salt-polyamine hardeners disclosed are given in the following examples:

EXAMPLE 17

An amine complex "A" of calcium chloride and ethylene diamine was prepared by mixing 55.5 parts by weight of anhydrous, finely powdered calcium chloride with 30.0 parts by weight of diamine at room temperature. The mixture was agitated to form an intimate dispersion. Agitation was continued until the liquid phase disappeared and a dry powder which was somewhat caked appeared. The temperature of the mixture at the commencement of agitation increased rapidly, indicating that reaction was occurring, and fell gradually as the powder formed and the liquid phase disappeared. The molar ratio of CaCl_2 to ethylene diamine was 1:1, so that the reaction product corresponded to the empirical formula



15.4 grams of the product thus obtained were dispersed in 100 grams of liquid epoxy resin of the epichlorohydrin-bisphenol of acetone type, having a viscosity of about 130 poises (25° C.), an epoxide equivalent of about 200, and a melting point in the range of about 8–12° C.

To this dispersion, there were then added 9.7 grams of water, this weight being that stoichiometrically required for formation of the $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ hydrate. During mixing the odor of ethylene diamine was evident, and after 24 hours, the mass had solidified.

EXAMPLE 18

100 weight parts of the liquid epoxy resin described

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in Example 17 were mixed with 233 parts by weight of fine sand and 40 parts by weight of silicon dioxide aerogel. The silica dioxide aerogel had a particle size in the range of 0.5 to 3.0 microns and a specific surface area of 200 square meters per gram. The function of the addition of the sand, which had a particle size between about 16 and 300 mesh, and the silica aerogel is that of converting the liquid polymers into the form of a free-flowing powder.

The following powder mixture is prepared:

15 weight parts of the complex amine "A" of Example 17.
373 weight parts of the resin powder prepared above.

The resulting mixture was a free-flowing powder, remarkable stable upon long term storage, even though the epoxy resin and hardener were in intimate contact with one another.

When water is added to this powder a fluid, coherent mix was obtained. This mix is spread onto a wooden floor surface at a thickness of approximately $\frac{3}{32}$ " and used as a setting bed for ceramic tile. After a period of 24 hours the material hardens and a strong bond developed between the wooden surface and the underside of the tile.

EXAMPLE 19

A composition similar to that described in Example 17 was prepared, but using 34.5 grams of diethylene triamine in place of the 30.0 grams of ethylene diamine in Example 17. Comparable results were obtained.

EXAMPLE 20

Example 17 was repeated, with the exception that 37.5 grams of tetraethylene pentamine were used in place of the 30.0 grams of ethylene diamine of Example 17. Comparable results were obtained.

Although specific forms of epoxy resin systems have been described for use in the present invention, it should be understood that other epoxy resins having the physical properties described hereinabove may also be used.

The method of installing ceramic tile on wood or wood products to give the improved constructions disclosed herein is as follows:

The wood is nailed, or otherwise held in position, as it would be in normal construction practices, except that open joints are left between boards, sheets, or planks. The width of the joint can be from $\frac{1}{16}$ " to $\frac{1}{2}$ ", but $\frac{1}{8}$ " to $\frac{1}{4}$ " is a more practical range for approximately $\frac{1}{2}$ " thick boards. All joints are backed by joists, studs, cats, subflooring, or sheeting. The epoxy resin adhesive as disclosed hereinabove is prepared and floated over the area to be filed or otherwise covered with component surfacing material, and forced into the open joints between boards. The adhesive is gauged by drawing a notched trowel through the floated layer and removing excess adhesive if there is any. The tile, or other surfacing material is laid on the troweled adhesive and fixed in place to form a level and true surface. After a proper curing time, usually twenty-four hours, an epoxy resin adhesive similar to or the same as the mortar adhesive, but in any event possessing the properties disclosed hereinabove, is forced between the tile or component surfacing material to fill the joints and be level with the finished floor surface. The cured installation thus achieved meets all the claims of this invention.

The method of installing ceramic tile or other component surfacing material on old wood installations is similar. New boards may or may not be applied to the old wood surface depending on the condition of the old wood surface. When old wood is to be directly covered, the adhesive is applied as a thin float coat and forced into all openings in the old wood surface. The procedure

from that point on is the same as for new wood surface as described previously.

The thickness of the adhesive used is not restricted except from a practical viewpoint. Thickness from $\frac{1}{16}$ " to $\frac{1}{4}$ " have proven equally satisfactory in performance tests.

The following examples illustrate the method of preparing the new construction materials disclosed herein and the unexpected properties thereof. Although specific, it should be understood that these examples are not intended to restrict the scope of the present invention, except as such limitations may appear in the claims.

EXAMPLE 21

Fir plywood $\frac{5}{8}$ " thick was applied over 2" wide joists spaced 16" on center. Resin coated nails were used every 8" on the studs. Joints in the plywood layer were left open $\frac{1}{4}$ ". The adhesive composition prepared according to Example 9 was forced between the plywood sheets in the $\frac{1}{4}$ " open joint, and spread on the plywood surface with a $\frac{3}{16}$ " square notched trowel, giving an average mortar thickness of $\frac{3}{32}$ ".

Square edge porcelain ceramic tile, $1\frac{1}{2}$ " x $1\frac{1}{2}$ ", pre-mounted with paper on the face of 1' x 2' sheets were laid on the mortar and beat to level. After twenty-four hours, the paper was removed from the face of the tile and the same adhesive composition was applied to the tile surface and forced into the joints between the tiles. Excess epoxy resin adhesive composition was cleaned from the tile surface with a sponge wetted by plain water. The cured floor section was tested for strength and durability after seven days aging.

As a comparison, another installation was produced using the same technique, with the exception that a mortar prepared from organic adhesive was substituted for the epoxy resin adhesive composition.

In tests performed simultaneously on the two constructed panels, the panels were subjected to three hours of heavy rubber wheel traffic and three hours of steel wheel traffic in that order, using a Robinson Floor Tester.

The tile installation with the epoxy resin adhesive of Example 9 survived the entire test with practically no damage. Only minor chips at tile edges occurred which were not visible at 5' from the floor surface. There were no structural damage.

The installation laid and grouted with organic adhesive was severely damaged at the end of rubber wheel test and was completely destroyed after ten minutes of steel wheel traffic.

EXAMPLE 22

Example 21 is a repeated with the exception that 2" x 2" cushion edged, natural clay ceramic tile pre-mounted with paper on the face of 1' x 2' sheets are substituted for the porcelain ceramic tile of Example 21. Similar results are obtained.

EXAMPLE 23

Example 21 was repeated with the exception that $4\frac{1}{4}$ " x $4\frac{1}{4}$ " cushion edged, glazed adsorptive ceramic tile laid singly, were substituted for the porcelain ceramic tile of Example 21. Similar results were obtained.

EXAMPLE 24

Example 21 was repeated with the exception that 6" x 6" x $\frac{1}{2}$ " and 6" x 3" x $\frac{1}{2}$ " red quarry tile, laid singly, were substituted for the porcelain ceramic tile of Example 21. Similar results were obtained.

EXAMPLE 25

Floor panels prepared according to Example 21 and using the tile disclosed therein, and various bonding materials were prepared and tested for impact resistance. The results of the tests are indicated in Table I.

Table I

	Construction details	Panel	Condition	(In.-lbs.)
5	Tile set and grouted with epoxy resin of Example 9 on $\frac{5}{8}$ " thick plywood.	1	First damage...	18
	Tile set and grouted with CTA-12 on $\frac{5}{8}$ " thick plywood.	2	-----do-----	9
10	Tile set and grouted conventionally in Portland cement.	3	-----do-----	$2\frac{1}{2}$

The data in Table I were obtained by dropping a 2" diameter steel ball onto the firmly seated tile installations. As is readily apparent, the amount of impact that can be withstood by the construction of the present invention (Panel 1) is considerably higher than that that could be withstood by Panels 2 and 3.

EXAMPLE 26

A 4' x 4' floor was installed by laying plywood on wooden joists. The flooring was divided into four equal sections, and covered with $1\frac{1}{2}$ " square porcelain, square edged tile following the procedure of Example 21, and using the bonding materials specified in Table II.

Table II

	Mortar	Grout
30	Quadrant No. 1.... Epoxy resin adhesive of Example 9.	Epoxy resin adhesive of Example 9.
	Quadrant No. 2.... do-----	PC: Sand.
	Quadrant No. 3.... CTA-12-----	PC: Sand.
35	Quadrant No. 4.... CTA-12-----	Epoxy resin adhesive of Example 9.

In Table I and II, "CTA-12" refers to the organic adhesive referred to hereinabove and supplied by Minnesota Mining and Manufacturing Co.

After permitting the floor to stand for 7 days, it was tested with a Robinson Floor Tester.

The test schedule was as follows: 1 hour of rubber wheel traffic with a load of 80 lbs. per wheel; 1 hour of rubber wheel traffic with a load of 160 lbs. per wheel; 1 hour of rubber wheel traffic with a load of 240 lbs. per wheel. A repeat of the above with steel wheels substituted for the rubber wheels.

The only quadrant to survive the entire rubber wheel test was quadrant No. 1 which used the epoxy resin adhesive of Example 9 for both laying and grouting the tile. There was absolutely no damage to this area.

In quadrant No. 2 the Portland cement:sand grout was partially destroyed by the flexing action of the floor. No tile was damaged.

In quadrant No. 3 the grout in the wheel path was completely destroyed (powdered). No tile was damaged.

In quadrant No. 4 with CTA-12 adhesive and the epoxy resin of Example 9 used as a grout, the tile were broken at the edges (first damage noted during the first hour). The strong grout exerted such unyielding pressure on the tile as the plywood flexed that the tile flaked, or spalled, at many joints.

The most interesting observation made was that the tile set with the epoxy resin adhesive of Example 9 reinforced the plywood sufficiently to cut the deflection between joints in half for that quadrant. Thus, the epoxy resin set and grouted quadrant No. 1 flexed less than half the amount that quadrant No. 4 did.

The condition of each quadrant after one hour of steel wheels with a load of 80 lbs. and one-half hour of steel wheels with a load of 160 lbs. was as follows:

Quadrant No. 1.—All grout and all tile were intact. Some tile showed flaws at corners which were the beginning of vertical cracks through the tile. No tile or grout was loose or pitted.

Quadrant No. 2.—The Portland cement:sand grout was powdered in all joints in the wheel path. Tile edges were crumbled and powdered so that joints between tiles were $\frac{1}{8}$ " to $\frac{1}{4}$ " wide. No tile was cracked and the bond to the epoxy resin adhesive was intact.

Quadrant No. 3.—Tile and grout in the wheel path were completely disintegrated. Plywood showed through in most parts and the surface veneer on the plywood was cut and splintered.

Quadrant No. 4.—The tile was all broken into small pieces, with many pieces dislodged. The epoxy resin grout was almost perfectly intact forming a grid between the broken tile pieces.

EXAMPLE 27

Flooring constructions produced according to the procedure of Example 21 were prepared and tested for strength. For comparison purposes, various bonding materials were used, as indicated in Table III.

The thickness of the plywood used in the tests was $\frac{3}{8}$ ". The results of these tests are summarized in Table III.

Table III

Construction details			Load deflection constant (lbs./in.)	Deflection at failure (in.)
Mortar		Grout type		
Thickness	Type			
Control (Plain 3/8" no tile).		Thick plywood	1,050	0.33
3/8"	CTA-12	PC: Sand	1,000	0.35
3/8"	CTA-12	Epoxy resin 2	1,051	0.39
1/16"	Epoxy resin 1	do	2,900	0.30
3/8"	do	do	3,100	0.38
1/8"	do	do	3,900	0.35
1/4"	do	do	4,000	0.31
1/16"	do	Epoxy resin 1	4,000	0.34
3/8"	do	do	4,500	0.30
1/8"	do	do	5,000	0.35
1/4"	do	do	4,900	0.35

¹ Epoxy resin produced according to Example 9.

² Epoxy resin produced according to Example 10.

In Table III, load deflection constants are listed for various combinations of mortar, grout, tile and plywood. The data were obtained using 3" wide samples with tile applied as noted in the table. The tiles were porcelain ceramic tile, $1\frac{1}{16}$ " square, square edged, $\frac{3}{16}$ " thick. The test specimens were loaded at their mid-point and supported on knife edges 16" apart. The deflection was measured at the mid-point of the sample.

The data in Table III is sufficient to calculate actual capacities of a floor installed by the techniques disclosed herein and using epoxy resin mortars and grouts having the properties described. The calculations, on the basis of supported spans between joints 16" on center (the most conservative consideration) indicates that flooring produced according to the teachings contained herein have a maximum deflection of 0.0075" when the floor is loaded at 200 pounds per sq. ft. The calculation for a concentrated load is more approximate. It indicates less than $\frac{1}{32}$ " deflection for a 200 pound concentrated load at a point mid-way between joints.

In installing ceramic tile on plywood according to the teachings of the present invention, it has found to be advantageous to employ a special but simple construction technique.

The plywood sheets are assembled with $\frac{1}{4}$ " to $\frac{1}{2}$ " wide open joints between them. These open joints are then filled with the epoxy resin adhesive compositions of the type disclosed herein or at the time the adhesive compositions are being applied to the floor surfaces to receive the tile.

Tests made for joint strength and tile damage at joints have proved this method to be superior to that in which tight joints with or without reinforcing is employed.

The preferred assembly provides a continuous floor layer which will not permit localized movement to damage the tile surface.

The advantages of using the preferred type of construction are shown in the following example:

EXAMPLE 28

Test samples were made of 3" wide plywood strips $\frac{3}{8}$ " thick jointed in the center of their length, and covered on one side with ceramic mosaic tile installed following the procedures of Example 21, and using the adhesive prepared according to Example 9. Three different joint constructions were used. The assemblies were strained intentionally along the longitudinal axes until failure occurred. The results of the tests are tabulated below in Table IV. The joint construction in each of the test panels is described in the table. The ultimate tension force in Table III is an average of 4 runs.

Table IV

Test No.	Joint construction	Ultimate tension, force-lbs.
1-----	Plain butt plywood joint, middle of tile over wood joint.	910
2-----	Plain butt plywood joint, tile joint over wood joint.	454
3-----	Steel fly screen over plain butt joint, middle of tile over wood joint.	1,026
4-----	Steel fly screen over plain butt joint, tile joint over wood joint.	760
5-----	$\frac{1}{2}$ " wide open plywood joint, middle of tile over wood joint. $\frac{1}{2}$ " joint filled with epoxy resin adhesive.	2,205
6-----	$\frac{1}{2}$ " wide open plywood joint, tile joint over wood joint. $\frac{1}{2}$ " joint filled with epoxy resin adhesive.	2,093

The preferred method of constructing the floorings described herein using a plywood substrata was used in Test Nos. 5 and 6. The ultimate tension force for the joint construction of Tests 5 and 6 is considerably higher than the ultimate tension strength for joint constructions of Tests 1 to 4, inclusive, as will readily be apparent from Table IV.

The invention will be further clarified by a reading of the following description in conjunction with the drawing, in which:

FIG. 1 is a vertical section, partially broken away, through a wooden floor having ceramic tile bonded thereto with the epoxy resin disclosed herein;

FIG. 2 is a cross section of the flooring of the preferred embodiment of the present invention, showing the pieces of wood with spaced joints;

FIG. 3 is a cross section of a flooring having a construction slightly different from that shown in FIG. 2.

As shown in FIG. 1, a wooden floor 2 is overlaid with an epoxy resin adhesive composition 4 and ceramic tile 6. The adhesive resin composition bonds the ceramic tile to the wooden substrata. The spaces between the tile are also filled with epoxy resin 8.

FIG. 2 shows a preferred embodiment of the present invention in which pieces of the wooden floor, such as plywood 12, are laid with wide open joints 14 between them. The epoxy resin composition 16 covers the flooring and fills the open joints between the boards. The ceramic tile 20 is laid over the wooden joint with the middle of the tile bridging the joints. Epoxy resin also fills the joints 22 between the tiles.

FIGURE 2(a) shows a section of the FIGURE 2 embodiment taken through a joist 30 which supports wooden pieces 12.

FIG. 3 shows a construction which is the same as that in FIG. 2 with the exception that the ceramic tiles are laid such that the tile joint is over the wood joint.

EXAMPLE 29

This example illustrates a three-part epoxy resin system which may be used in the present invention.

The following resin-base was prepared:

63.5 weight parts of epoxide resin
26.7 weight parts of polystyrene resin
5.5 weight parts of phenyl glycidyl ether
1.3 weight parts of (2,2' bis(-hydroxyphenyl) propane)

and mixed with the following hardener portion:

37.3 weight parts amido-amino tall oil resin, equivalent weight of 135, viscosity at 25° C. of 250 centipoises.
1.2 weight parts diethylene triamine.

After thorough mixing was added the following filler portion which yielded a trowelable material:

285.0 weight parts sand (through 30 mesh screen)
9.3 weight parts silica aerogel
.15 weight parts carbon black

The epoxide resin was of the epichlorohydrin bisphenol of acetone type described in Example 1.

The resulting adhesive was used in place of the adhesive of Example 9 in the tests reported in Examples 21 and 26. Similar results were obtained.

EXAMPLE 30

Counter-top panels were prepared by overlaying a plywood sheet $\frac{5}{8}$ " thick with ceramic tile; the tile used was porcelain ceramic tile, $1\frac{1}{2}$ " x $1\frac{1}{2}$ " premounted on the face of 1' x 2' sheets. The sheets were laid on the mortar indicated in Table V and beat to level. After twenty-four hours, the paper was removed from the face of the tile and the joints between tiles grouted, as indicated in Table V.

The resulting counter-tops were tested for resiliency by the Marble Drop Test. The results of the test are reported in Table V.

Table V

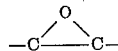
Construction	Construction details	Percent rebound of glass marble after free fall
1.....	Tile set and grouted with epoxy resin of Example 9 on $\frac{5}{8}$ " thick plywood.	27
2.....	Tile set and grouted with CTA-12 on $\frac{5}{8}$ " thick plywood.	28
3.....	Tile set and grouted conventionally in Portland cement.	87

Based on the performance cited elsewhere in this application of ceramic tile installed in epoxy thin-set on plywood, on the Robinson Floor Tester, one would expect the resiliency of the assembly of construction 1 of Table V to be very high. In other words, one would expect a ceramic or glass marble when dropped on such a surface to rebound without losing much of its kinetic energy to the tile. When a glass marble is dropped on a conventional assembly, i.e., construction 3 of Table V, it rebounds to nearly the same height from which it was dropped and if not deflected will continue to bounce several times. If the same marble is dropped on a soft carpet, for example, it does not bounce but stops dead because all the kinetic energy is absorbed. Likewise, if it is dropped on a ceramic tile floor installed by an organic adhesive such as CTA-12, i.e., construction 2 of Table V, it rebounds very little or not at all. This is because the kinetic energy is absorbed and dissipated in the adhesive or other members. The floor does not have the elastic capacity to keep the kinetic energy in the bouncing marble. So, while the ceramic tile installed by the epoxy has the durability of ceramic tile installed in the conventional way by Portland cement, it lacks the elastic resiliency shown by this system. On the other hand, and this is most surprising and was unexpected, it absorbs impact energy very similar to the manner of ceramic tile installations using organic adhesives. Of course, as shown elsewhere, organic adhesive installed tile lacks durability on the Robinson Floor Tester, as has already been shown.

The invention in its broader aspects is not limited to the specific methods, compositions and constructions described, but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed:

1. An improved structural member comprising wood and ceramic tile in combination, and having enhanced load bearing capacity, wear resistance, and impact resistance, said member comprising a plurality of wooden pieces aligned in spaced relationship so as to leave spaces therebetween; means adjacent one surface of said wooden pieces for supporting said pieces and maintaining them in aligned spaced relationship; a cured epoxy resin mortar bed covering a second surface of said wooden pieces and extending into and filling the spaces therebetween; and a plurality of ceramic tile pieces set in said cured epoxy resin mortar bed in spaced edge to edge relationship and bonded to the wooden pieces thereby; said ceramic tile pieces having grout between their edges; said cured epoxy resin mortar bed being formed by curing an epoxy resin adhesive composition which comprises a resinous epoxide characterized by a reactive



group; between about 5 and 400 percent by weight, based upon the weight of resinous epoxide, of an inert, finely divided filler having an average particle size ranging between about 5 and 500 mesh; and an epoxy resin hardener capable of entering into a cross-linking reaction with the resinous epoxide to cure and harden the same; said cured epoxy resin mortar bed having a compressive stress of at least 3000 p.s.i.; an elastic modulus of at least 0.05×10^6 ; a tensile strength at least $\frac{1}{5}$ of the compressive strength and being substantially non-shrinking; and forming a bond between the wooden boards and the ceramic tile which has a strength in excess of 400 p.s.i. measured as shear.

2. The improved structural member of claim 1 wherein the epoxy resin hardener is an amino amide formed by reacting a polyamine compound with a carboxylic acid compound.

3. The structural member of claim 1 wherein the grout between the edges of the ceramic tile pieces is a cured epoxy resin adhesive composition.

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4. The improved structural member of claim 1 wherein the ceramic tiles straddle the spaces between the wooden pieces.

5. The improved structural member of claim 1 wherein the spaces between the tile are over the spaces between the wooden pieces.

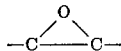
6. The improved structural member of claim 1 wherein the resinous epoxide comprises between about 0.5 and 15 percent water, based upon the weight of the resinous epoxide.

7. The improved structural member of claim 1 wherein the hardener comprises a dry mixture of an acid salt of a polyfunctional amine and a strong base, the dry mixture being activatable upon addition of a polar solvent.

8. The improved structural member of claim 1 wherein the hardener comprises a dry mixture of a stable amine complex of a metal salt and a polyamine, the salt having a cation capable of forming a stable complex with an amino group.

9. The method of claim 1 wherein the cured epoxy resin has an elastic modulus of at least 0.5×10^6 .

10. The method of enhancing the load bearing capacity, wear resistance, and impact resistance of a structural member comprising, in combination, ceramic tile and wood, which comprises: preparing a wooden substrata by aligning a plurality of wooden pieces in spaced relationship on a plurality of support members so that the wooden pieces straddle the support members; covering the wooden pieces with a mortar bed of an epoxy resin adhesive composition, the epoxy resin adhesive composition extending into and filling the spaces between the wooden pieces; said adhesive composition comprising: a resinous epoxide characterized by a reactive



group; between about 5 and 400 percent by weight, based upon the weight of resinous epoxide, of an inert, finely divided filler having an average particle size ranging between about 5 and 500 mesh; and an epoxy resin hardener capable of entering into a cross-linking reaction with the resinous epoxide to cure and harden the same; setting a plurality of ceramic tile pieces in the mortar bed in spaced edge to edge relationship; grouting the spaces between the ceramic tile pieces; and allowing the mortar

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bed to harden, to thereby provide a bond strength between the wooden pieces and the ceramic tile in excess of 400 p.s.i. measured as shear; the epoxy resin adhesive employed being such that the cured resin has a compressive stress of at least 3000 p.s.i.; an elastic modulus of at least 0.05×10^6 ; a tensile strength at least $\frac{1}{5}$ of the compressive strength; and being substantially non-shrinking.

11. The method of claim 10 wherein the ceramic tiles are laid so as to straddle the spaces between the wooden pieces.

12. The method of claim 10 wherein the ceramic tiles are laid so that spaces between the tiles are over the spaces between the wooden pieces.

13. The method of claim 10 including the step of filling the spaces between the tile with an epoxy resin adhesive.

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