

SPECIFICATION

METHOD OF FABRICATING A MEMBRANOUS SUBSTANCE AND METHOD OF
FABRICATING A MULTILAYER MEMBRANOUS SUBSTANCE

TECHNICAL FIELD

The present invention relates to a method of fabricating a membranous substance and a methods of fabricating a multilayer membranous substance to be used in flooring materials in buildings and so forth.

BACKGROUND OF THE ART

Room floors within buildings, in particular floors to be used in flooring warehouses, are generally prepared by forming a multilayer resin film on concrete. For example, a resin film is first formed on concrete for the purpose of protecting concrete, among others, by applying an epoxy-based resin or a methyl methacrylate-based resin, for instance, and then further forming, on that film, a urethane resin film for the purpose of attaining a good appearance and/or non-slip and/or other properties by applying an aggregate-containing urethane curable resin, whereby a multilayer film is obtained. However, such a method has problems. Namely, it uses an organic solvent in the step of application and this causes environmental pollution. In addition, the progress of curing is slow, hence a long term of construction is required. Furthermore, the multilayer film obtained is very hard and lacking in flexibility, so that a further problem arises, namely the film cannot keep pace with the expansion and contraction of concrete but may crack. Further durability problems from the concrete protection viewpoint are that when a heavy article is placed or moved on the floor surface, the film surface may readily be damaged and crack, and that when an edged tool or a like sharp-edged article falls thereon, the

film may crack and the resulting damage may extend to the substrate concrete.

Japanese Kokai Publication 2000-225376 discloses a method of forming a composite organic membranous substance which uses a reticulate or bar-like material and a solvent-free two-component curable resin. According to this publication, the solvent-free two-component curable resin of the ultrafast curing type is applied to the reticulate or bar-like material in the manner of two-component collision-mixing spray and thus causing curing to unite the resin with the reticulate or bar-like material. The composite organic membranous substances obtained by this method have flexibility.

However, such solvent-free two-component ultrafast curable resin generates a considerable amount of heat on the occasion of curing, so that the reticulate or bar-like material, which serves as part of the substrate, may be deformed and the membranous substance obtained may be unsatisfactory in smoothness. For concealing such deformation, the resin must be used in large amounts.

Accordingly, it is an object of the present invention to provide a method of fabricating a membranous substance and a method of fabricating a multilayer membranous substance excellent in smoothness, impact resistance and durability even when they are relatively thin.

SUMMARY OF THE INVENTION

The present invention provides a method of fabricating a membranous substance

which comprises (1) a step of fixing a reinforcing material onto a substrate surface and (2) a step of forming the membranous substance on said substrate by applying a solvent-free two-component polyurea curable resin (A) in such manner that said reinforcing material is embedded in the resin throughout from said substrate surface side. The

solvent-free two-component polyurea curable resin (A) preferably comprises a polyamine component and a polyisocyanate component,

said polyamine component comprising not less than 50% by weight of an aromatic polyamine (a-1) having a polyalkylene chain or a polyoxyalkylene chain with an amine equivalent of 400 to 800 and not more than 15% by weight of a polyoxyalkylenepolyamine (a-2) having at least two aliphatic amino groups in a molecule with an amine equivalent of 80 to 300.

The aromatic polyamine (a-1) is, for example, a primary aromatic polyamine, and the polyoxyalkylenepolyamine (a-2) is, for example, a primary polyoxyalkylenediamine.

The application in the step (2) is carried out, for example, in the manner of spread coating. The substrate is, for example, concrete.

The present invention also provides a membranous substance obtainable by the above-mentioned method of fabricating.

The present invention further provides a method of fabricating a multilayer membranous substance

which comprises (3) a step of forming a membranous substance onto the membranous substance mentioned above by applying a solvent-free two-component ultrafast curable resin (B) in the manner of two-component collision-mixing spray coating followed by curing.

Such solvent-free two-component ultrafast curable resin (B) is, for example, a solvent-free two-component polyurethane curable resin, a solvent-free two-component polyurethane/polyurea curable resin or a solvent-free two-component polyurea curable resin containing a polyamine component and/or a polyol component, together with a polyisocyanate component. The two-component collision-mixing spray coating in the step (3) is carried out while

each of the two components of the solvent-free two-component ultrafast curable resin (B) is warmed to a temperature not lower than 40°C.

The solvent-free two-component ultrafast curable resin (B) has a tack-free curing time not longer than 3 minutes.

The present invention further provides a multilayer membranous substance obtainable by the above-mentioned method of fabricating.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the first step in the method of fabricating a membranous substance according to the present invention, a reinforcing material is fixed to the surface of a substrate. The above substrate is not particularly restricted but includes those used in structural parts of buildings and the like. Concrete or mortar is preferred, however. The above substrate surface may have a primer film. The above primer film is not particularly restricted but includes those obtainable by applying any of those primers well known in the art.

The above-mentioned reinforcing material is not particularly restricted but includes, for example, reticulate materials and bar-like materials. Specifically, these reinforcing materials may be made of a metal such as iron, aluminum or stainless steel, an inorganic fibrous material such as glass fibers and carbon fibers, an organic fibrous material such as aramide fibers, various synthetic resins such as polyvinyl chloride, polyethylene or polyester, various natural materials such as vegetable fibers, or the like.

The method of fixing the above reinforcing material to the above substrate surface is not particularly restricted but is preferably the method by which the structure thereof can be maintained in the next and

subsequent steps. Thus, for example, the substrate may be provided with supporting members in order to fix the reinforcing material thereon. In view of the thickness of coating of the solvent-free two-component polyurea curable resin (A) in the next step, the above substrate and the above reinforcing material are preferably cohered with each other. If they are not cohered, it will become necessary to apply the solvent-free two-component polyurea curable resin (A) thickly in the next step for embedding the reinforcing material therein; this is uneconomical.

Further, the height from the substrate surface to the surface of the reinforcing material which is opposite to the substrate side is preferably not more than 20 mm. If the above height is in excess of 20 mm, it is also necessary to apply the solvent-free two-component polyurea curable resin (A) thickly in the next step for embedding the reinforcing material therein; this is uneconomical.

In the second step of the method of fabricating a membranous substance according to the invention, the solvent-free two-component polyurea curable resin (A) is applied in such manner that the reinforcing material obtained in the above step (1) is embedded in the resin throughout from the substrate surface side to thereby form a composite substance on the substrate.

The method for the above application/embedding is not particularly restricted but preferably is a spread coating comprising manual spreading using a trowel or spatula, for instance. The coating film thickness is not particularly restricted but is required to be such that the above reinforcing material is embedded. If the above reinforcing material is not fully embedded, the resulting membranous substance will be unsatisfactory in smoothness. The coating film thickness mentioned above can be selected according to the intended use. Generally, however, it is 2 to 20 mm. If the above coating film thickness is less than

2 mm, it will be difficult to sufficiently embed the above reinforcing material. If it exceeds 20 mm, the above solvent-free two-component polyurea curable resin (A) will uneconomically be required in increased amounts.

Thereafter, the above solvent-free two-component polyurea curable resin (A) cures to a tack-free state in a certain period to give the desired membranous substance.

The curing time until a tack-free state of the solvent-free two-component polyurea curable resin (A) to be used in the method of fabricating a membranous substance in accordance with the invention is not particularly restricted but preferably is 30 minutes to 3 hours from the viewpoint of sufficient time for application and of reduction in time of construction. If the above curing time until a tack-free state is shorter than 30 minutes, the organic membranous substance obtained will be unsatisfactory in smoothness and, if it is longer than 3 hours, the time of construction may possibly be prolonged. The curing time until a tack-free state so referred to herein means the curing time required until no fingerprint remains upon pressing a finger onto the resin applied.

The thus-obtained membranous substance is cohered to the substrate surface. The film thickness thereof is not particularly restricted but is, for example, 2 to 20 mm.

The above solvent-free two-component polyurea curing type resin (A) comprises a polyamine component and a polyisocyanate component. The above polyamine component preferably comprises an aromatic polyamine (a-1) having a polyalkylene chain or a polyoxyalkylene chain with an amine equivalent of 400 to 800 and a polyoxyalkylenepolyamine (a-2) having at least two aliphatic amino groups in a molecule with an amine equivalent of 80 to 300, for instance. The above aromatic polyamine (a-1) is a component retarding the curing rate while the above polyoxyalkylenepolyamine (a-2) is a component accelerating the curing rate.

If the above aromatic polyamine (a-1) has an amine equivalent less than 400, the curing rate of the resin composition will be too rapid, so that a sufficient time for application will not be secured. If it exceeds 800, the curing rate will become excessively slow, making it impossible to control the curing time. An amine equivalent of 500 to 700 is preferred.

The above aromatic polyamine (a-1) is not particularly restricted but includes, for example, polyethylene glycol bis(4-aminobenzoate), polyethylene glycol bis(2-aminobenzoate), polyethylene glycol bis(3-aminobenzoate), polytetramethylene glycol bis(4-aminobenzoate), polytetramethylene glycol bis(2-aminobenzoate), polypropylene glycol bis(4-aminobenzoate), polypropylene glycol bis(2-aminobenzoate), poly(oxyethylene-oxypropylene) glycol bis(4-aminobenzoate), poly(oxyethylene-propylene ether) glycol bis(4-aminobenzoate), polyoxybutylene glycol bis(4-aminobenzoate), polytetramethylene glycol bis(3,5-diaminobenzoate), polypropylene ether glycerol tris(4-aminobenzoate), polypropylene ether pentaerythritol tetrakis(4-aminobenzoate), polyoxyethylenebis(4-aminobenzamide), polyoxypropylenebis(4-aminobenzamide), polyoxybutylene glycol bis(4-aminobenzoate), polyoxypropylenebis(3,5-diaminobenzamide) and the like. Two or more of these may be used in combination. The above aromatic polyamine (a-1) preferably has at least two primary amino groups bound to an aromatic ring in a molecule from the viewpoint of reactivity and of physical characteristics of membranous substances obtained.

Preferred as the aromatic polyamine (a-1) to be contained in the polyamine component of the above solvent-free two-component polyurea curable resin (A) from the reactivity viewpoint are polytetramethylene glycol bis(4-aminobenzoate), polypropylene glycol bis(4-aminobenzoate),

poly(oxyethylene-propylene ether) glycol bis(4-aminobenzoate) and polyoxybutylene glycol bis(4-aminobenzoate). Commercially available as such polyamine are, for example, Elasma 1000 (amine equivalent about 620), Elasma 1000P (amine equivalent about 550) and Polea SL-100A (amine equivalent about 590; all three being products of Ihara Chemical Industry Co., Ltd.).

If, on the other hand, the amine equivalent of the polyoxyalkylene polyamine (a-2) contained in the polyamine component of the above solvent-free two-component polyurea curable resin (A) is less than 80, the curing rate is excessively high to cause a heterogeneous reaction within the membranous substance, so that the physical characteristics of the membranous substance obtained will be markedly deteriorated. If it exceeds 300, marked increase in viscosity and gelling will result due to the increase in molecular weight and it will become difficult to secure a sufficient time for application. An amine equivalent of 100 to 200 is preferred.

The above polyoxyalkylenepolyamine (a-2) is not particularly restricted but includes, for example, those derived from polyoxyalkylene polyols by reacting the terminal hydroxyl groups thereof with ammonia under high-temperature and high-pressure conditions using a hydrogenation-dehydrogenation catalyst. Such polyoxyalkylenepolyamines (a-2) may contain, as impurities, polyoxyalkylene polyols remaining unreacted with ammonia.

The above polyoxyalkylenepolyamine (a-2) is preferably one having a primary amino group(s) in a molecule in view of the reaction rate with the isocyanato group. From the viewpoint of the hardness of the membranous substance obtained, polyoxyalkylenepolyamines having at least two primary amino groups mentioned above in a molecule are more preferred. As products commercially available as such, there may be mentioned, for example,

Jeffamine D-230 (amine equivalent about 120) and Jeffamine D-400 (amine equivalent about 200; both being products of Huntsman Specialty Chemicals).

The polyamine component to be contained in the above solvent-free two-component polyurea curable resin (A) comprises, for example, not less than 50% by weight of the above-mentioned aromatic polyamine (a-1) and not more than 15% by weight of the above-mentioned polyoxyalkylenepolyamine (a-2). When the content of the above aromatic polyamine (a-1) is less than 50% by weight, a decreased level of toughness will result. A preferred content is not less than 70% by weight. When the content of the above polyoxyalkylenepolyamine (a-2) is in excess of 15% by weight, the curing rate becomes high, rendering it impossible to secure a sufficient time for application.

The above polyamine component may contain other polyamines than the above-mentioned aromatic polyamine (a-1) and the above-mentioned polyoxyalkylenepolyamine (a-2). Such other polyamines are not particularly restricted but include, for example, diethyltoluenediamine, toluenediamine, xylylenediamine and like aromatic polyamines and aliphatic polyamines.

On the other hand, the polyisocyanate component to be contained in the above solvent-free two-component polyurea curable resin (A) is not particularly restricted but may be any of those polyisocyanate compounds known in the art. Thus, for example, there may be mentioned aromatic polyisocyanate compounds, aliphatic polyisocyanate compounds, alicyclic polyisocyanate compounds and so on. The above aromatic polyisocyanate compounds are not particularly restricted but include, for example, liquid diphenylmethanediisocyanate or diphenylmethanediisocyanate partial prepolymers obtainable by carbodiimide modification; 2,4-tolylene diisocyanate (2,4-TDI), diphenylmethane-4,4'-diisocyanate (MDI), diphenylmethane-

2,4'-diisocyanate, xylylene diisocyanate (XDI), crude tolylene diisocyanate, polymethylenepolyphenylisocyanate and carbodiimide modification of these; biuret modifications thereof; and prepolymer modifications thereof. The above aliphatic polyisocyanate compounds and alicyclic polyisocyanate compounds are not particularly restricted, but includes, for example, dicyclohexylmethane-4,4'-diisocyanate, isophoronediiisocyanate, hexamethylene diisocyanate and isocyanurate modifications, carbodiimide modifications and prepolymer modifications of these,

Preferred as the polyisocyanate component to be contained in the solvent-free two-component polyurea curable resin (A) for use in the method of fabricating a membranous substance of the present invention from the viewpoint of curability and of adhesiveness are dipheylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, prepolymers or modifications of these and like aromatic polyisocyanate compounds.

As commercial products available as such isocyanate component, there may be mentioned, for example, Millionate MLT (product of Nippon Polyurethane Industry), Millionate MTL-S (product of Nippon Polyurethane Industry) and Coronate MX (product of Nippon Polyurethane Industry).

Where necessary, the solvent-free two-component polyurea curable resin (A) may further contain, in addition to the above components, an additive(s) such as surfactants, foaming agents, foam stabilizers, flame retardants, plasticizers, dyes, fillers, fungicides, bactericides, various reinforcing agents, internal mold release agents, antioxidants, weather stabilizers and the like. These additives may be added to a mixture of the above-mentioned polyamine component and the above-mentioned polyisocyanate component or may be added in advance to respective components.

The mixing ratio between the above polyamine

component and the above polyisocyanate component in such solvent-free two-component polyurea curable resin (A) is preferably 0.7 to 1.5 as expressed in terms of the equivalent ratio of the isocyanato groups in the above polyisocyanate component to the amino groups in the above polyamine component. If the above equivalent ratio is outside the above range, the membranous substance obtained may have unsatisfactory characteristics or may possibly remain sticky. A range from 0.95 to 1.25 is more preferred and a range from 1.01 to 1.10 is still more preferred. In addition, by adjusting the content of the above aromatic polyamine (a-1) in the above polyamine component, it is possible to adjust the curing time until a tack-free state. For example, a curing time of 30 minutes to 3 hours can be attained.

From the pot life viewpoint, the above solvent-free two-component polyurea curable resin (A) is preferably prepared by mixing the above polyamine component and the above polyisocyanate component together just prior to application using a two-component mixing apparatus, a Disper agitator or the like, or by manual blending.

The method of fabricating a multilayer membranous substance according to the invention further comprises, as the third step, (3) a step of forming an organic membranous substance onto the membranous substance obtainable by the above-mentioned method of fabricating a membranous substance by applying a solvent-free two-component ultrafast curable (B) in the manner of two-component collision-mixing spray coating followed by curing.

The method of application in the manner of two-component collision-mixing spray coating as mentioned above comprises spraying two components of the solvent-free two-component ultrafast curable (B) so as to cause collision and mixing of two components with each other. In this step, the curing reaction proceeds to a certain extent while

particles sprayed are still in a scattered state. For the above application in the manner of two-component collision-mixing spray coating, a high-pressure two-component collision-mixing spray system is preferably used.

The above-mentioned high-pressure two-component collision-mixing spray system is not particularly restricted but includes, for example, such proportion units as H-2000, H-3500 and FF-1600 (all being products of Gusmer, U.S.A.) and a Model HF-100 two-component high-pressure delivery mixing machine (product of Toho Machinery Industry, Japan) and the like. As high-pressure two-component collision-mixing spray guns having a mechanical self-cleaning function, there may be mentioned the GX-7 gun and GX-7-400 gun (both being products of Gusmer, U.S.A.) and the like and, as such guns equipped with an air cleaning function, there may be mentioned the Propeller gun (product of Glass-Craft, U.S.A.) and the like. From the applicability viewpoint, the above two components are preferably warmed to a temperature at which their viscosity can be satisfactorily maintained at a level enabling spraying/atomizing of the same, for example to a temperature not lower than 40°C. The coating film thickness is not particularly restricted but can appropriately be selected according to the intended use, generally within the range of 2 to 20 mm.

Since it cures very rapidly, the above solvent-free two-component ultrafast curable resin (B) is preferably prepared by mixing up on the occasion of the above-mentioned application in the manner of two-component collision-mixing spray coating.

The curing time until a tack-free state of such solvent-free two-component ultrafast curable (B) can be adjusted according to the above polyol component species and the amount thereof as well as the species of plasticizers and the like other component(s) and the

amount(s) thereof. The time is, for example, preferably not longer than 3 minutes, more preferably not longer than 20 seconds.

The film thickness of the thus-obtained multilayer membranous substance is not particularly restricted but preferably is 4 to 40 mm.

The solvent-free two-component ultrafast curable resin (B) to be used in the method of fabricating a multilayer membranous substance of the present invention is, for example, the solvent-free, two-component polyurethane curable type, two-component polyurethane/polyurea curable type or two-component polyurea curable type containing a polyamine component and/or a polyol component, together with a polyisocyanate component.

The polyamine component mentioned above preferably comprises, for example, a polyoxyalkylenepolyamine (a-3) and an active aromatic diamine (a-4) having no electron-attracting group on the aromatic nucleus and having an alkyl substituent containing not more than 5 carbon atoms at a position adjacent to the amino group, exclusive of toluenediamine.

As the above polyoxyalkylenepolyamine (a-3), those having at least two aliphatic amino groups in a molecule and having an amine equivalent of 800 to 3000 are preferred.

As commercial products available as such polyoxyalkylenepolyamine (a-3), there may be mentioned, for example, such polyoxypropylenediamines as Jeffamine D-2000 (product of Huntsman Specialty Chemicals, amine equivalent about 1,000); and such polyoxypropylenetriamines as Tecslim TR-5050 (product of Huntsman Specialty Chemicals, amine equivalent about 1,930), etc.

Also usable are modified polyoxyalkylenepolyamines derived from the above polyoxyalkylene polyamines (a-3) by converting at least some of the primary amino groups thereof to a secondary amino group(s) by the Michael

addition reaction with an unsaturated hydrocarbon compound represented by the general formula $\text{CH}_2=\text{C}(\text{R})-\text{Y}$ (in which R represents a hydrogen atom or a methyl group and Y represents an electron-attracting group). The electron-attracting group represented by the above Y is not particularly restricted but includes, for example, ester residues, ketone residues, cyano residues, substituted or unsubstituted amido residues, sulfonic acid residues, sulfonic acid ester residues and the like. The above-mentioned unsaturated hydrocarbon compound is not particularly restricted but includes, for example, acrylate esters such as n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, 2-ethylhexyl acrylate, methyl acrylate, lauryl acrylate, stearyl acrylate and propyl acrylate; methacrylate esters such as n-butyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, lauryl methacrylate, stearyl methacrylate and propyl methacrylate; acrylonitrile; acrylamide; N,N'-dimethylacrylamide; ethyl vinyl sulfone; methyl vinylsulfonate, ethyl vinylsulfonate, etc.

As the active aromatic diamine (a-4) having no electron-attracting group on the aromatic nucleus and having an alkyl substituent containing not more than 5 carbon atoms at a position adjacent to the amino group, exclusive of toluenediamine, there may specifically be mentioned 1,3-dimethyl-2,4-diaminobenzene, 1,3-diethyl-2,4-diaminobenzene, 1,3-dimethyl-2,6-diaminobenzene, 1,4-diethyl-2,5-diaminobenzene, 1,4-diisopropyl-2,5-diaminobenzene, 1,4-dibutyl-2,5-diaminobenzene, 1,3,5-triethyl-2,4-diaminobenzene, 1,3,5-triethyl-2,6-diaminobenzene, 1,3,5-tripropyl-2,6-diaminobenzene, 1-methyl-3,5-diethyl-2,4-diaminobenzene, 1-methyl-3,5-diethyl-2,6-diaminobenzene and the like. Two or more of these may be used in combination. As commercial products

of such, there may be mentioned Ethacure 100 (product of Albemarle Corporation) and the like.

Also suited for use are modified polyamines derived from the above active aromatic diamines (a-4) having no electron-attracting group on the aromatic nucleus and having an alkyl substituent containing not more than 5 carbon atoms in a position adjacent to the amino group, exclusive of toluenediamine, by converting at least some of the primary amino groups thereof to a secondary amino group(s) by the Michael addition reaction with the above-mentioned unsaturated hydrocarbon compound.

The weight ratio between the above polyoxyalkylenepolyamine (a-3) and the active aromatic diamine (a-4) having no electron-attracting group on the aromatic nucleus and having an alkyl substituent containing not more than 5 carbon atoms in a position adjacent to the amino group, exclusive of toluenediamine in the polyamine component to be contained in the above solvent-free two-component ultrafast curable resin (B) is preferably 20/3 to 1/1. If the above weight ratio exceeds 20/3, the membranous substance obtained will become extremely soft and show semitackiness. If it is less than 1/1, the membranous substance obtained will be excessively hard and may possibly become brittle. A range of 5/1 to 5/2 is more preferred.

The above-mentioned polyol component is not particularly restricted but preferably comprises a low-molecular-weight one having a number average molecular weight of less than 1,000 and a high-molecular-weight one having a number average molecular weight of 1,000 to about 10,000 so that the membranous substance obtained may be satisfactory in hardness and physical properties.

The above low-molecular-weight polyol may be a polyether polyol or a polyester polyol, for instance. The above polyether polyol includes, for example, polyols such

as ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, trimethylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,2-hexyl glycol, 1,10-decanediol, 1,2-cyclohexanediol, glycerol, 1,2,6-hexanetriol, 1,1,1-trimethylolethane and 1,1,1-trimethylolpropane; products derived from a polyhydric alcohol such as pentaerythritol by addition polymerization of at least one epoxide such as ethylene oxide, propylene oxide, butylene oxide or tetrahydrofuran.

As the above polyester polyol, there may be mentioned various polyester polyols producible by reacting an aliphatic dibasic acid with an aliphatic glycol, as well as polycaprolactone polyol and the like. As such polyester polyols, there may be mentioned reaction products of those polyether polyols mentioned hereinabove or a mixture thereof with a polycarboxylic acid, in particular a dicarboxylic acid, or an ester-forming derivative thereof, for example succinic acid, glutaric acid or adipic acid, or the dimethyl ester thereof, sebacic acid, phthalic anhydride, tetrachlorophthalic anhydride or dimethyl terephthalate. Mention may also be made of those obtainable by subjecting a cyclic ester, namely a lactone such as caprolactone to ring opening addition polymerization with a polyol.

On the other hand, the polyisocyanate component to be contained in the above solvent-free two-component ultrafast curable resin (B) is not particularly restricted but there may specifically be mentioned those mentioned hereinabove referring to the solvent-free two-component polyurea curable resin (A).

Where necessary, the above solvent-free two-component ultrafast curable resin (B) may further contain, in addition to the components mentioned above, an additive(s) each selected from among surfactants, foaming agents, foam stabilizers, flame retardants, plasticizers, dyes, fillers,

fungicides, bactericides, various reinforcing agents, internal mold release agents, antioxidants, weather stabilizers and the like. These additives may be added to the above-mentioned polyamine component and/or polyol component, or to the polyisocyanate component.

The membranous substance and multilayer membranous substance obtained respectively by the method of fabricating a membranous substance and the method of fabricating a multilayer membranous substance of the present invention are high in corrosion resistance, smoothness and impact resistance and, therefore, are particularly suited for use as flooring materials in buildings such as concrete or mortar and the like.

The method of fabricating a membranous substance according to the present invention, which comprises the step of disposing a reinforcing material and the step of forming a membranous substance using a specific solvent-free two-component curable resin, gives membranous substances excellent in smoothness and impact resistance even when they are relatively thin. A sufficient time for application can be secured and, in addition, no solvent evaporates, so that the term of construction can be shortened and the possibility of environmental pollution can be reduced.

Furthermore, the multilayer membranous substance obtained by forming a further membranous substance on the membranous substance obtained using a specific solvent-free two-component curable resin different from the one used first can have further improved impact resistance and durability.

Such membranous substances or multilayer membranous substances can have excellent smoothness, impact resistance and durability even when they are thin and, therefore, the amounts of raw materials required can be reduced very

economically.

The membranous substances and multilayer membranous substances provided by the invention are suited for use as flooring materials in buildings. Since the term of construction is very short, they are applicable also in recoating, repair, etc.

EXAMPLES

Production Example 1: Preparation of a solvent-free two-component polyurea curable resin (A)

A solvent-free two-component polyurea curable resin (A) was prepared by stirring and mixing 167 weight parts of Elasma 1000P (aromatic polyamine, product of Ihara Chemical Industry Co., Ltd.), 14 weight parts of Jeffamine D-230 (polyoxyalkylenepolyamine, product of Huntsman Specialty Chemicals), 190 weight parts of MDI prepolymer (polyisocyanate, isocyanate equivalent about 270) and 3 weight parts of Ethacure 100 (active aromatic diamine, product of Albemarle Corporation) in a static mixer. The polyurea curable resin obtained was substantially free of any solvent. This polyurea curable resin showed a curing time of 90 minutes until a tack-free state.

Example 1

A substrate was prepared by applying Tough Guard R-M primer (one-component moisture-curable primer, product of Nippon paint) to a JIS sidewalk concrete flag (300 x 300 x 70 mm) to a coating weight of 0.15 kg/m². A reticulate material, namely a mesh made of stainless steel wires with a diameter of 1 mm and having a mesh size of 10 mm, was disposed on the substrate horizontally cohered therewith and unmovably fixed by using anchors.

Then, the solvent-free two-component polyurea curable resin (A) obtained in Production Example 1 was applied in such manner that the reticulate material is embedded

throughout from the substrate surface side while controlling a film thickness to about 5 mm. After the subsequent 16 hours of standing, a test panel with a membranous substance formed on the substrate was obtained. The time required for the whole process was 24 hours.

Example 2

A membranous substance was formed in the same manner as in Example 1 except that the solvent-free two-component polyurea curable resin obtained in Production Example 1 was applied by spreading for embedding the reticulate material therein while controlling a film thickness to about 2 mm. Further, onto the above substance, a polyamine component: a mixture of 70 weight parts of Jeffamine D-2000 (polyether polyamine, product of Huntsman Specialty Chemicals) and 30 weight parts of Ethacure 100, and a polyisocyanate component: an isocyanate prepolymer obtained by reacting, by mixing, 57 weight parts of Millionate MTL (MDI, product of Nippon Polyurethane Industry) and 55 weight parts of Newpol PP-3000 (polypropylene oxide, product of Sanyo Kasei Co.) were applied, while warming each component to about 55°C, to a film thickness of about 3 mm using an H-3500 spray system and a GX-7 gun (two-component mixing spray system, both being products of Gusmer, U.S.A.), to give a membranous substance comprising a solvent-free two-component polyurea curable resin (B). The subsequent 14 hours of standing gave a test panel with the thus-formed multilayer membranous substance. The time required for the whole process was 24 hours.

Comparative Example 1

A test panel with a membranous substance formed thereon was obtained in the same manner as in Example 1 except that no reticulate material was disposed nor fixed on the substrate. The time required for the whole process

was 20 hours.

Comparative Example 2

A test panel with a membranous substance formed thereon was obtained in the same manner as in Example 2 except that the solvent-free two-component polyurea curable resin (A) obtained in Production Example 1 was not applied but that the solvent-free two-component polyurea curable resin (B) was directly applied to the substrate. The time required for the whole process was 18 hours.

Comparative Example 3

A test panel with a multilayer membranous substance formed thereon was obtained in the same manner as in Example 2 except that a solvent-borne two-component epoxy curable resin was applied in lieu of the solvent-free two-component polyurea curable resin (A) obtained in Production Example 1, followed by 14 days of standing. The time required for the whole process was 15 days.

Comparative Example 4

A test panel with a multilayer membranous substance formed thereon was obtained in the same manner as in Comparative Example 3 except that no reticulate material was disposed and fixed on the substrate. The time required for the whole process was 15 days.

Evaluation tests

The test panels with a membranous substance formed thereon as obtained in Example 1 and Comparative Examples 1 and 2 as well as the test panels with a multilayer membranous substance formed thereon as obtained in Example 2 and Comparative Examples 3 and 4 were subjected to the following evaluation tests. The respective evaluation results are shown in Table 1.

<Smoothness>

Each test panel was evaluated for smoothness by visual observation. The evaluation criteria were as follows.

○: Smooth without unevenness

△: Marked unevenness

×: Failure to completely embed the reticulate material

<Impact resistance>

Each test panel was evaluated for the condition after subjecting the same to DuPont drop testing (test conditions: load 2 kg, vertical dropping from a height of 2 m, 1/2 inch semispherical impactor). The evaluation criteria were as follows.

○: Indentation in the membranous substance or multilayer membranous substance

△: Cracking in the membranous substance or multilayer membranous substance

×: Cracking in the membranous substance or multilayer membranous substance, together with cracking in the substrate

<Penetration resistance>

A SUS 420J2 stainless steel kitchen knife (total weight 330 g) was allowed to drop onto each test panel obtained from a height of 2 m with the edge directed downward and thereafter the test panel was evaluated. The evaluation criteria were as follows.

○: Damaging only in the surface layer of the membranous substance or multilayer membranous substance

△: Cracking throughout the membranous substance or multilayer membranous substance

×: Cracking throughout the membranous substance or multilayer membranous substance, with further damaging in

the substrate

Table 1

	Ex. 1	Ex. 2	Compar. Ex. 1	Compar. Ex. 2	Compar. Ex. 3	Compar. Ex. 4
Smoothness	○	○	○	×	○	○
Impact resistance	○	○	○	○	△	×
Penetration resistance	○	○	×	○	△	×
Whole process time	24 hrs.	24 hrs.	20 hrs.	18 hrs.	15 days	15 days

As is evident from Table 1, the membranous substances according to the invention were excellent in smoothness, impact resistance and durability but, when no reinforcing material was used or when the ultrafast curable resin was applied directly to the reinforcing material, the impact resistance or smoothness decreased respectively. When the organic solvent-containing system was applied, the curing proceeded with the evaporation of the organic solvent and, thus, a time of construction was prolonged.



CLAIMS

1. A method of fabricating a membranous substance which comprises (1) a step of fixing a reinforcing material onto a substrate surface and (2) a step of forming the membranous substance on said substrate by applying a solvent-free two-component polyurea curable resin (A) in such manner that said reinforcing material is embedded in the resin throughout from said substrate surface side.

2. The method of fabricating a membranous substance according to Claim 1,

wherein said solvent-free two-component polyurea curable resin (A) comprises a polyamine component and a polyisocyanate component,

said polyamine component comprising not less than 50% by weight of an aromatic polyamine (a-1) having a polyalkylene chain or a polyoxyalkylene chain with an amine equivalent of 400 to 800 and not more than 15% by weight of a polyoxyalkylenepolyamine (a-2) having at least two aliphatic amino groups in a molecule with an amine equivalent of 80 to 300.

3. The method of fabricating a membranous substance according to Claim 2,

wherein said aromatic polyamine (a-1) is a primary aromatic polyamine.

4. The method of fabricating a membranous substance according to Claim 2 or 3,

wherein said polyoxyalkylenepolyamine (a-2) is a primary polyoxyalkylenediamine.

5. The method of fabricating a membranous substance according to any of Claims 1 to 4,



wherein said substrate is concrete.

6. A membranous substance obtainable by the method of fabricating a membranous substance according to any of Claims 1 to 5.

7. A method of fabricating a multilayer membranous substance

which comprises (3) a step of forming a membranous substance onto the membranous substance according to Claim 6 by applying a solvent-free two-component ultrafast curable resin (B) in the manner of two-component collision-mixing spray coating followed by curing.

8. The method of fabricating a multilayer membranous substance according to Claim 7,

wherein said solvent-free two-component ultrafast curable resin (B) is a solvent-free two-component polyurethane curable resin, a solvent-free two-component polyurethane/polyurea curable resin or a solvent-free two-component polyurea curable resin containing a polyamine component and/or a polyol component, together with a polyisocyanate component.

9. The method of fabricating a multilayer membranous substance according to Claim 8,

wherein the two-component collision-mixing spray coating in said step (3) is carried out while each of the two components of said solvent-free two-component ultrafast curable resin (B) is warmed to a temperature not lower than 40°C.

10. The method of fabricating a multilayer membranous substance according to any of Claims 7 to 9,

wherein said solvent-free two-component ultrafast



curable resin (B) has a tack-free curing time not longer than 3 minutes.

11. A multilayer membranous substance obtainable by
5 the method of fabricating a multilayer membranous substance
according to any of Claims 7 to 10.