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METAL PLATE-BONDED CONCRETE AND METHOD FOR BONDING A
METAL PLATE AND A CONCRETE ✓

The present invention relates to a metal plate-bonded concrete which is a structure reinforced by bonding a
5 metal plate to a concrete.

For the purpose of reinforcing a concrete structure, a method is used which comprises attaching a reinforcing member such as a steel material to a concrete anew. Particularly, a reinforcing method is used which
10 comprises bonding a metal plate to a concrete. In this case, it is important that the strength of the metal plate-bonded concrete is high. As the reinforcing method, there may be mentioned (1) a process which comprises attaching a steel plate as a reinforcing member
15 to a floor plate, a beam, a bent or a handrail and unifying them by means of an adhesive (steel plate bonding reinforcing process), or (2) a process which comprises attaching a steel beam as a reinforcing member to a floor plate and unifying them by means of an
20 adhesive (beam-adding reinforcing process) [Industrial

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materials, vol. 41, No. 12, 188-193 (1993 special edition)].

As an adhesive to be used for these reinforcing methods, an epoxy resin adhesive has been used. The
5 epoxy resin adhesive may, for example, be a one pack type adhesive comprising an epoxy resin adhesive as the main agent and dicyandiamide or the like as a curing agent, or a two pack type adhesive using an amine or a polyamide as a curing agent.

10 However, the one pack type adhesive has had drawbacks that heating is required for curing, and it is difficult to use it for bonding with a concrete structure to be reinforced. The two pack type adhesive has had drawbacks that to prevent curing failure, complete mixing with a
15 constant mixing ratio with the curing agent is required, the application control is cumbersome, and curing at a low temperature is poor.

To overcome such drawbacks, an acrylic resin adhesive containing a cold setting acrylic resin composition has
20 been used instead of the epoxy resin adhesive. A (meth)acrylic resin adhesive is disclosed in JP-B-58-19707.

The acrylic resin adhesive has a good low temperature curing property and a wide range of the mixing ratio
25 within which adequate adhesive strength can be obtained, whereby the application control is easy. Further, the acrylic resin adhesive is excellent in the adhesive

property under a wet condition or a dry condition, or to a surface having a hydrophobic nature and thus has a merit that a step for primer treatment of the surface of a substrate such as a metal plate or concrete, which was
5 necessary with an epoxy resin adhesive, can be eliminated. However, it has had a drawback that when used for bonding a concrete, the bond strength is low.

With respect to an acrylic resin adhesive having improved bond strength to a concrete, JP-B-60-19789
10 discloses an acrylic resin adhesive comprising a (meth)acrylic monomer, a butadiene oligomer having (meth)acryl-modified terminals, an organic peroxide and a cobalt salt of an organic acid/ a metal organic chelate compound.

15 However, when a metal plate-bonded concrete is prepared by using this acrylic resin adhesive, there are the following drawbacks (1) and (2), whereby the metal plate is likely to peel from the concrete, and such an adhesive is hardly useful for a process for reinforcing a
20 concrete.

(1) When dissimilar materials such as a metal plate and a concrete, are bonded, the adhesive force at the interface between the metal and the concrete is weak, whereby the bond strength will be low.

25 (2) The metal plate-bonded concrete is poor in water resistance, and when exposed to moisture such as rain water or humidity, the bond strength will be lowered by

the moisture such as humidity, whereby the metal plate is likely to peel from the concrete.

The present inventors have conducted extensive studies to solve these problems and as a result, have
5 found that by using a specific primer, it is possible to obtain a metal plate-bonded concrete which has high bond strength between dissimilar materials such as a metal plate and a concrete and which has water resistance so that the bond strength will not be lowered by moisture
10 such as humidity. The present invention has been accomplished on the basis of this discovery.

Namely, the present invention provides:

1. A metal plate-bonded concrete which comprises a concrete having its surface impregnated with a primer
15 comprising (a) a (meth)acrylate having an ethylenically unsaturated double bond in its molecule, (b) a polymerization initiator and (c) an activator, and a metal plate bonded to the concrete surface by an acrylic resin adhesive.
- 20 2. The metal plate-bonded concrete according to Item 1, wherein the (meth)acrylate (a) in the primer is a (meth)acrylate having an ethylenically unsaturated double bond which is not adjacent to a carbonyl group in its molecule.
- 25 3. The metal plate-bonded concrete according to Item 1, wherein the (meth)acrylate (a) in the primer is a monofunctional (meth)acrylate having an ethylenically

unsaturated double bond in its molecule.

4. The metal plate-bonded concrete according to Item 1, wherein the (meth)acrylate (a) in the primer is a polyfunctional (meth)acrylate having an ethylenically unsaturated double bond in its molecule.

5. The metal plate-bonded concrete according to any one of Items 1 to 4, wherein the activator (c) in the primer contains a metal salt of an organic acid and/or a metal organic chelate compound.

6. The metal plate-bonded concrete according to any one of Items 1 to 5, wherein the primer contains (d) a (meth)acrylate having no ethylenically unsaturated double bond in its molecule.

7. The metal plate-bonded concrete according to any one of Items 1 to 6, wherein the surface of the metal plate is made of zinc.

8. The metal plate-bonded concrete according to any one of Items 1 to 6, wherein the surface of the metal plate is made of stainless steel.

Further, the present invention provides:

9. A method for bonding a metal plate and a concrete, which comprises impregnating a concrete surface with a primer comprising (a) a (meth)acrylate having an ethylenically unsaturated double bond in its molecule, (b) a polymerization initiator and (c) an activator, and then bonding a metal plate to the concrete surface by an acrylic resin adhesive.

10. A primer which comprises (a) a (meth)acrylate having an ethylenically unsaturated double bond in its molecule, (b) a polymerization initiator and (c) an activator, and which is impregnated into a concrete surface prior to bonding a metal plate to the concrete surface by an acrylic resin adhesive.

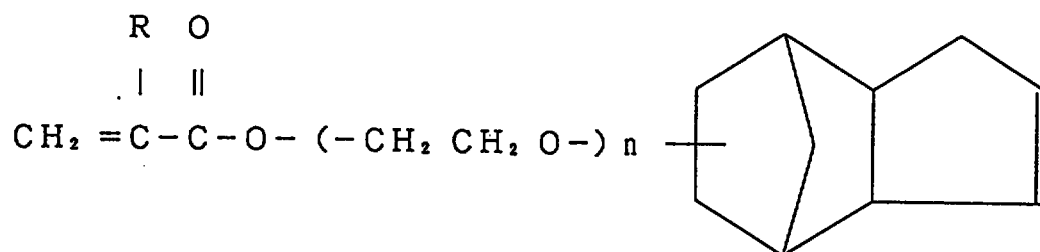
Now, the present invention will be described in detail.

The (meth)acrylate having an ethylenically unsaturated double bond in its molecule as component (a) to be used in the present invention is a (meth)acrylate having an ethylenically unsaturated double bond in its molecule and having at least one methacryloyl or acryloyl group in its molecule. Here, the ethylenically unsaturated double bond is meant for an ethylenically unsaturated double bond which is not adjacent (conjugated) to a carbonyl group, and is not a so-called α , β -unsaturated carbonyl group. By this component (a) it is possible to attain high bond strength between dissimilar materials such as a metal plate and a concrete and to obtain an effect of water resistance such that the bond strength will not be lowered by moisture such as humidity.

The component (a) may, for example, be a monofunctional (meth)acrylate having an ethylenically unsaturated double bond in its molecule, or a polyfunctional (meth)acrylate having an ethylenically

unsaturated double bond in its molecule. These two types may be used in combination.

The monofunctional (meth)acrylate having an ethylenically unsaturated double bond in its molecule has an effect such that molecular designing to adjust the bond strength, the curing rate, etc. can thereby be facilitated. As such a monofunctional (meth)acrylate, a (meth)acrylate having a dicyclopentenyl group, of the following formula, is preferred from the viewpoint of the bond strength and the curing rate.



15

In the above formula, R is hydrogen or a methyl group, and n is an integer of 0 or 1. The compound of the above formula may, for example, be dicyclopentenyl acrylate, dicyclopentenyl methacrylate, dicyclopentenyl-oxyethyl acrylate or dicyclopentenyl-oxyethyl methacrylate.

The polyfunctional (meth)acrylate having an ethylenically unsaturated double bond in its molecule has an effect that the bond strength will thereby be improved even with a small amount. Such a polyfunctional (meth)acrylate may, for example, be a both terminal methacryl-modified liquid polybutadiene ("TE-2000",

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manufactured by Nippon Soda Co., Ltd.), a both terminal acryl-modified liquid polyacrylonitrile butadiene ("HycarVTBNX", manufactured by Ube Industries, Ltd.), a both terminal methacryl-modified liquid partially
5 hydrogenated polybutadiene ("TEAI-1000", manufactured by Nippon Soda Co., Ltd.), or a both terminal acryl-modified liquid polybutadiene ("BAC-45", manufactured by Osaka Yuki K.K.)

Among polyfunctional (meth)acrylates having an
10 ethylenically unsaturated double bond, the both terminal (meth)acryl-modified butadiene oligomer is preferred from the viewpoint of the bond strength and the curing rate. The both terminal (meth)acryl-modified butadiene oligomer is a copolymer or polymer of butadiene having
15 (meth)acryloyl groups at its both terminals, which has an average molecular weight of from 1000 to 10000.

The both terminal (meth)acryl-modified butadiene oligomer may be produced, for example, as follows. A polyfunctional (meth)acrylate having a 1,2-polybutadiene
20 backbone in its molecule can be obtained, for example, by reacting a diisocyanate compound to an oligomer of a 1,2-polybutadiene with hydroxyl group terminals, obtained by living anion polymerization, and then reacting a (meth)acrylate having a hydroxyl group, such as 2-
25 hydroxyethyl (meth)acrylate, to the remaining isocyanate groups.

Component (a) is used preferably in an amount of from

1 to 95 parts by weight, more preferably from 5 to 80 parts by weight, per 100 parts by weight of the sum of component (a) and component (d) which will be described hereinafter. If the amount is less than 1 part by weight, the bond strength or the water resistance is likely to be low. If it exceeds 95 parts by weight, the viscosity tends to be too high, whereby the operation efficiency will be low, or the cured product tends to be so hard that the bond strength will decrease.

10 The polymerization initiator as component (b) to be used in the present invention is a substance which serves as a so-called radical polymerization initiator. For example, the following organic peroxides may be mentioned.

15 (1) Ketone peroxides, such as methyl ethyl ketone peroxide, cyclohexanone peroxide, 3,3,5-trimethylcyclohexanone peroxide, methylcyclohexanone peroxide, methylacetoacetate peroxide, and acetylacetone peroxide.

20 (2) Peroxyketals, such as 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(tert-butylperoxy)cyclohexane, 2,2-bis(tert-butylperoxy)octane, n-butyl-4,4-bis(tert-butylperoxy)valerate, and 2,2-bis(tert-butylperoxy)butane.

25 (3) Hydroperoxides, such as tert-butyl hydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, paramenthane hydroperoxide, 2,5-dimethylhexane-2,5-

dihydroperoxide, and 1,1,3,3-tetramethylbutyl hydroperoxide.

(4) Dialkyl peroxides, such as di-tert-butyl peroxide, tert-butylcumyl peroxide, dicumyl peroxide,
5 α,α' -bis(tert-butylperoxy-m-isopropyl)benzene, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, and 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3.

(5) Diacyl peroxides, such as acetyl peroxide, isobutyl peroxide, octanoyl peroxide, decanoyl peroxide,
10 laurynoyl peroxide, 3,3,5-trimethylhexanoyl peroxide, succinic acid peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, and m-toluoyl peroxide.

(6) Peroxydicarbonates, such as diisopropyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, di-
15 n-propyl peroxydicarbonate, bis(4-tert-butylcyclohexyl) peroxydicarbonate, di-2-ethoxyethyl peroxydicarbonate, dimethoxyisopropyl peroxydicarbonate, di(3-methyl-3-methoxybutyl) peroxydicarbonate, and diallyl peroxydicarbonate.

20 (7) Peroxyesters, such as tert-butyl peroxyacetate, tert-butyl peroxyisobutylate, tert-butyl peroxy-pivalate, tert-butyl peroxyneodecanoate, cumyl peroxyneodecanoate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxy-3,3,5-trimethyl hexanoate, tert-butyl peroxy-laurate,
25 tert-butyl peroxybenzoate, di-tert-butyl peroxyisophthalate, 2,5-dimethyl-2,5-di(benzoyl peroxy) hexane, tert-butyl peroxy maleic acid, tert-butyl

peroxyisopropylcarbonate, cumyl peroxyoctoate, tert-hexyl peroxyneodecanoate, tert-hexyl peroxy-pivalate, tert-butyl peroxyneo-hexanoate, tert-hexyl peroxyneo-hexanoate, and cumyl peroxyneo-hexanoate.

- 5 (8) Other organic peroxides, such as acetylcyclohexylsulfonyl peroxide, and tert-butyl peroxyallylcarbonate.

As polymerization initiators other than organic peroxides, the following azo compounds may, for example,
10 be mentioned.

- (1) Azonitrile compounds, such as azobisisobutyronitrile, 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 1,1'-azobis(cyclohexane-1-carbonitrile), 1-[(1-cyano-1-methylethyl)azo]formamide,
15 and 2-phenylazo-4-methoxy-2,4-dimethylvaleronitrile.

(2) Azoamidine compounds, such as 2,2'-azobis(2-methylpropioneamidine) dihydrochloride.

(3) Cyclic azoamidine compounds, such as 2,2'-azobis[2-(2-imidazoline-2-yl)propane].

- 20 (4) Azoamide compounds, such as 2,2'-azobis{2-methyl-n-[1,1-bis(hydroxymethyl)-2-hydroxyethyl] propioneamide}, and 2,2'-azobis{2-methyl-n-[1,1-bis(hydroxymethyl)ethyl] propioneamide.

(5) Alkylazo compounds, such as 2,2'-azobis(2,4,4-trimethylpentane).
25

These polymerization initiators may be used alone or in combination as a mixture of two or more of them.

Among the polymerization initiators, an organic peroxide is preferred from the viewpoint of the bond strength and the curing rate.

Component (b) is used preferably in an amount of from
5 0.5 to 10 parts by weight, per 100 parts by weight of the sum of component (a) and component (d) which will be described hereinafter. If the amount is less than 0.5 part by weight, curing tends to be slow, and if it exceeds 10 parts by weight, no further improvement in
10 e.g. the curing rate will be obtained, and the metal plate tends to peel from the concrete.

The activator as component (c) to be used in the present invention is a compound which promotes the decomposition of the polymerization initiator. For
15 example, the following compounds may be mentioned.

(1) Thiourea derivatives, such as diethylthiourea, dibutylthiourea, ethylenethiourea, tetramethylthiourea, mercaptobenzimidazole, and benzoylthiourea.

(2) Amines, such as N,N-diethyl-p-toluidine, N,N-
20 dimethyl-p-toluidine, N,N-diisopropanol-p-toluidine, triethylamine, tripropylamine, ethyldiethanolamine, N,N-dimethylaniline, ethylene diamine, and triethanolamine.

(3) Metal salts of organic acids, such as cobalt naphthenate, copper naphthenate, zinc naphthenate, cobalt
25 octylate, and iron octylate.

(4) Organic metal chelate compounds, such as copper acetylacetonate, titanium acetylacetonate, manganese

acetylacetonate, chromium acetylacetonate, iron acetylacetonate, vanadyl acetylacetonate, and cobalt acetylacetonate.

5 The activator includes other compounds such as a condensation reaction product of an aldehyde with an amine. These activators may be used alone or in combination as a mixture of two or more of them.

Among them, a thiourea derivative, a metal salt of an organic acid or an organic metal chelate compound is preferred from the viewpoint of the curing property, and a metal salt of an organic acid and/or an organic metal chelate compound is more preferred with a view to improvement of the bond strength and the water resistance.

15 Component (c) is used preferably in an amount of from 0.1 to 10 parts by weight, per 100 parts by weight of component (a) and (d) which will be described hereinafter. If the amount is less than 0.1 part by weight, curing tends to be slow, and even if it exceeds 20 10 parts by weight, no further improvement in e.g. the curing rate will be obtained, and the metal plate rather tends to peel from the concrete.

The primer to be used in the present invention preferably contains (d) a (meth)acrylate having no ethylenically unsaturated double bond in its molecule. 25 By using the (meth)acrylate having no ethylenically unsaturated double bond in its molecule, the viscosity or

the curing rate can easily be adjusted.

The (meth)acrylate having no ethylenically unsaturated double bond in its molecule, may, for example, be (meth)acrylic acid, methyl (meth)acrylate, 5 ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isooctyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, phenyl (meth)acrylate, cyclohexyl (meth)acrylate, 10 dicyclopentanyl (meth)acrylate, isobornyl (meth)acrylate, methoxylated cyclodecatoriene (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, polyethylene glycol 15 mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, alkyloxypolyethylene glycol mono(meth)acrylate, alkyloxypolypropylene glycol mono(meth)acrylate, phenoxypolyethylene glycol mono(meth)acrylate, phenoxypolypropylene glycol 20 mono(meth)acrylate, tetrahydrofurfuryl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, glycidyl (meth)acrylate, caprolactone-modified tetrahydrofurfuryl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, N,N- 25 diethylaminoethyl (meth)acrylate, t-butylaminoethyl (meth)acrylate, morpholine (meth)acrylate, ethoxycarbonylmethyl (meth)acrylate, ethyleneoxide-

modified phthalic acid (meth)acrylate, ethyleneoxide-
modified succinic acid (meth)acrylate, trifluoroethyl
(meth)acrylate, tetrafluoropropyl (meth)acrylate, 2-
hydroxy-3-(meth)acryloyloxypropyltrimethylammonium
5 chloride, polyethylene glycol di(meth)acrylate,
polyglycerol di(meth)acrylate, polypropylene glycol
di(meth)acrylate, polybutylene glycol di(meth)acrylate,
1,4-butanediol di(meth)acrylate, 1,6-hexanediol
di(meth)acrylate, neopentyl glycol di(meth)acrylate,
10 trimethylolpropane tri(meth)acrylate, pentaerythritol
tetra(meth)acrylate, dipentaerythritol
hexa(meth)acrylate, tris(meth)acryloyloxyethyl
isocyanurate, 2,2-bis(4-(meth)acryloxyphenyl)propane,
2,2-bis(4-(meth)acryloxyethoxyphenyl)propane, 2,2-bis(4-
15 (meth)acryloxydiethoxyphenyl)propane, 2,2-bis(4-
(meth)acryloxypropoxyphenyl)propane, 2,2-bis(4-
(meth)acryloxytetraethoxyphenyl)propane, epoxy acrylate
"Viscoat #540", (manufactured by Osaka Yuki Kagaku Kogyo
K.K.), epoxy acrylate "Epoxy ester 3000M", (manufactured
20 by Kyoeisha Kagaku K.K.), polyester acrylate "Aronix M-
6100", (manufactured by Toa Gousei Chemical Industries
Co., Ltd.), or urethane acrylate "Aronix M-1100",
(manufactured by Toa Gousei Chemical Industries Co.,
Ltd.). These compounds may be used alone or in
25 combination as a mixture of two or more of them.

Among (meth)acrylate having no ethylenically
unsaturated double bond in its molecule, bisphenol A

diglycidyl ether di(meth)acrylate, methyl (meth)acrylate, and/or 2-hydroxyethyl (meth)acrylate, is preferred from the viewpoint of the viscosity, the curing rate, the bond strength and the water resistance.

5 Component (d) is used preferably in an amount of from 5 to 99 parts by weight, more preferably from 20 to 95 parts by weight, per 100 parts by weight of the sum of components (a) and (d). If the amount is less than 5 parts by weight, the viscosity tends to be high, whereby
10 the operation efficiency will be low, or the cured product tends to be so hard that the bond strength will be low. If it exceeds 95 parts by weight, the bond strength or the water resistance is likely to be low.

 Further, to the primer used in the present invention,
15 the various paraffins may be incorporated to facilitate curing of the part which is in contact with air. Such paraffins include, for example, a paraffin, microcrystalline wax, carnauba wax, bees wax, lanolin, spermaceti, ceresin and candelilla wax. Among them, a
20 paraffin is preferred. The melting point of such paraffins is preferably from 40 to 100°C.

 The paraffin is used preferably in an amount of from 0.1 to 5 parts by weight, per 100 parts by weight of the sum of component (a) and component (d). If the amount is
25 less than 0.1 part by weight, curing of the part which is in contact with air, tends to be poor, and if it exceeds 5 parts by weight, the bond strength tends to be low.

Further, for the purpose of improving the storage stability, various antioxidants, etc. including a polymerization inhibitor, may be used. The antioxidants include, for example, hydroquinone, hydroquinone monomethylether, 2,6-di-tert-butyl-p-cresol, 2,2'-methylene bis(4-methyl-6-tert-butylphenol), triphenyl phosphite, phenothiazine and N-isopropyl-N'-phenyl-p-phenylene diamine. Among them, hydroquinone monomethylether is preferred.

10 The antioxidant is used preferably in an amount of from 0.001 to 3 parts by weight, per 100 parts by weight of the sum of component (a) and component (d). If the amount is less than 0.001 part by weight, no substantial effects will be obtained, and if it exceeds 3 parts by
15 weight, the curing rate is likely to be low.

Further, for the purpose of adjusting the viscosity or the fluidity, various synthetic rubbers such as acrylonitrile-butadiene rubber (NBR), styrene-butadiene rubber, chloroprene rubber and butadiene rubber,
20 elastomer components such as natural rubber, thermoplastic polymers such as a methyl methacrylate-butadiene-styrene copolymer (MBS), a chlorosulfonated polyethylene, polyurethane, a styrene-acrylonitrile copolymer, an acrylonitrile-styrene-butadiene copolymer,
25 polymethylmethacrylate and linear polyurethane, and fine silica powder, may also be incorporated.

Furthermore, a known material such as a plasticizer,

a filler, a coloring agent or a rust-preventing agent may also be incorporated, as the case requires.

The acrylic resin adhesive to be used in the present invention is of a cold setting type and is not
5 particularly limited so long as it is an adhesive having (meth)acryloyl group in its molecule. However, it is preferred to incorporate a polymerization initiator and an activator, and an elastomer component. As is different from the primer, the acrylic resin adhesive to
10 be used in the present invention may not contain a (meth)acrylate having an ethylenically unsaturated double bond in its molecule.

The material for the metal plate to be used in the present invention is not particularly limited, and it may
15 be zinc, stainless steel, iron, galvanized sheet steel, bonde, copper, aluminum or an alloy thereof. From the viewpoint of the weather resistance or corrosion resistance, the surface of the metal plate is preferably zinc or stainless steel. When the surface of the metal
20 plate is zinc, economical efficiency is good, since the material is inexpensive. Whereas, when the metal plate is stainless steel, the appearance will be good.

The concrete to be used in the present invention, is not particularly limited, so long as it is a cement
25 concrete prepared by mixing cement, water, sand, gravel, and if necessary, flyash or a blast furnace slag.

The metal plate-bonded concrete to be used in the

present invention can be prepared as follows. A primer comprising components (a), (b) and (c), and optionally component (d), is prepared. The primer is coated uniformly in a thickness of from 0.01 to 1 mm on the concrete surface, and impregnated and cured. Then, the acrylic resin adhesive is uniformly coated on one or both of the concrete surface having the primer impregnated and cured and the metal plate surface, whereupon the concrete and the metal plate are bonded and cured to obtain a metal plate-bonded concrete. In a case where the primer is not impregnated into the concrete surface, the bond strength or the water resistance tends to be low, such being undesirable.

Coating of the primer composition and the acrylic resin adhesive used in the present invention, is carried out in the same manner as usual coating of a coating material, for example, by spray coating or brush coating.

As a practical embodiment for preparation of the primer used in the present invention, a method may, for example, be mentioned, wherein a one pack type primer storing all components essential to the primer except for the polymerization initiator and the activator, is prepared, and the polymerization initiator and the activator are added immediately prior to using the primer. As another embodiment, it may be used in the form of a two pack type primer. In the case of the two pack type, all components essential to the primer used in

the present invention are not mixed for storage. Namely, the primer or the adhesive agent composition is divided into a first liquid and a second liquid, and a polymerization initiator is incorporated to the first liquid and the activator is incorporated to the second liquid, so that they are separately stored. The two pack type is preferred from the viewpoint of the excellent storage stability. In this case, the two liquids may be used as a two pack type primer by simultaneously or separately coating them for contact and curing.

As practical embodiments of the acrylic resin adhesive to be used in the present invention, embodiments similar to the primer used in the present invention, may, for example, be mentioned.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to such specific Examples.

As test specimens, mortar specimens prepared in a size of 4 cm x 4 cm x 16 cm in accordance with JIS R 5201 and metal plates of 0.4 mm in thickness x 4 cm in width x 16 cm in length, were used.

Using commercial products, the respective components as identified in Tables 1 to 3 were mixed, to prepare primers and acrylic resin adhesives. Further, the following types of epoxy resin adhesives and metal plates were used.

Table 1

	Components	Composition Examples				
		1	2	3	4	5
Composi- tion (unit: parts by weight)	<u>Component (a)</u> Dicyclopentenyl- oxyethyl methacrylate	1	5	45	80	95
	<u>Component (b)</u> Cumene hydroperoxide	2	2	2	2	2
	<u>Component (c)</u> Cobalt octylate N,N-dimethyl-p- toluidine	1 1	1 1	1 1	1 1	1 1
	<u>Component (d)</u> 2-Hydroxyethyl methacrylate Bisphenol A diglycidyl ether diacrylate	9 90	9 86	5 50	2 18	1 4

Table 2

	Components	Composition Examples				
		6	7	8	9	10
Composi- tion (unit: parts by weight)	<u>Component (a)</u> Dicyclopentenyl- oxyethyl methacrylate TE-2000	100	1	5	50	80
	<u>Component (b)</u> Cumene hydroperoxide	2	2	2	2	2
	<u>Component (c)</u> Cobalt octylate Vanadyl acetylacetonate N,N-dimethyl-p- toluidine	1 1	3	3	3	3
	<u>Component (d)</u> 2-Hydroxyethyl methacrylate Methyl methacrylate		59 40	57 38	30 20	12 8

Table 3

	Components	Composition Examples			
		11	12	13	14
Composi- tion (unit: parts by weight)	<u>Component (a)</u> Dicyclopentenylloxyethyl methacrylate Dicyclopentenylloxyethyl acrylate TE-2000 TEAI-1000	95	45	50	
	<u>Component (b)</u> Cumene hydroperoxide	2	2	2	2
	<u>Component (c)</u> Cobalt octylate Vanadyl acetylacetonate Ethylene thiourea N,N-dimethyl-p-toluidine	3	1 1	3	3
	<u>Component (d)</u> 2-Hydroxyethyl methacrylate Methyl methacrylate Bisphenol A diglycidyl ether diacrylate	3 2	5 50	30 20	30 66 4
	<u>Other</u> NBR (nitrile content: 15%)				18

Materials used

Bisphenol A diglycidylether dimethacrylate:

Epoxyester 3000M, manufactured by Kyoeisha Kagaku K.K.

TE-2000: both terminal methacryl-modified liquid
5 polybutadiene, manufactured by Nippon Soda Co., Ltd.

TEAI-1000: both terminal methacryl-modified liquid
partially hydrogenated polybutadiene, manufactured by
Nippon Soda Co., Ltd.

NBR: commercially available acrylonitrile-butadiene
10 rubber (nitrile content: 15%)

Epoxy 1: epoxy resin adhesive (Bond E810,
manufactured by Konishi K.K.)

Epoxy 2: epoxy resin adhesive (Bond E2500,
manufactured by Konishi K.K.)

15 Epoxy 3: epoxy resin adhesive (FP-NS, manufactured by
Tonen K.K.)

Epoxy 4: epoxy resin adhesive (FR-E3P, manufactured
by Tonen K.K.)

Bonde: commercially available electro galvanized
20 steel plate

Galvanized sheet steel: commercially available hot
dip zinc-plated steel plate

Iron: commercially available cold rolled steel (SPCC
DD of JIS G 3141)

25 Stainless steel: commercially available cold rolled
stainless steel plate (SUS 304 of JIS G 4305)

EXAMPLES 1 to 24 and COMPARATIVE EXAMPLES 1 to 5

The primer of each of Examples and Comparative Examples shown in Tables 4 to 9, was coated in a thickness of about 0.3 mm on the mortar specimen by brush coating and left to stand at a temperature of 23°C under a humidity of 65% for 5 hours for impregnation and curing. Then, the acrylic resin adhesive as identified in Tables 4 to 9 was coated in a thickness of about 0.2 mm on the metal plate by brush coating, and the metal plate was bonded to the surface of the mortar specimen having the primer impregnated and cured, followed by curing to obtain a test specimen of a metal plate-bonded concrete.

With respect to this metal plate-bonded concrete, the four-point bending strength in an ordinary state and the four-point bending strength after a warm water resistance test, were measured. The four-point bending strength was measured at a load rate of 5 kgf/sec in accordance with the method for measuring bond strength prescribed in JIS R 6024, 4.8. However, for the measurement of the four-point bending strength, the test specimen of a metal plate-bonded concrete was placed so that the metal plate side was located below, and the metal plate was in contact with the supporting table of the testing machine for measuring the bend strength. In the case of the normal state, the metal plate-bonded concrete was aged at a temperature of 20°C under relative humidity of 65% for one week, whereupon the four-point bending strength was

measured. In the case of the measurement after the warm water resistance test, the metal plate-bonded concrete was immersed in a warm water of 60°C for one week, whereupon the four-point bending strength was measured.

- 5 The results are also shown in Tables 4 to 9. The unit for the four-point bending strength was kg/cm².

Table 4

	Components	Examples				
		1	2	3	4	5
Evaluation	Primer (Composition Example)	1	2	3	4	5
	Adhesive (Composition Example)	14	14	14	14	14
	Type of metal plate	Bonde	Bonde	Bonde	Bonde	Bonde
	Four-point bending strength (ordinary state)	213	221	232	224	214
	Four-point bending strength (after warm water resistance test)	206	215	230	216	207

Note: Unit of four-point bending strength: kgf/cm²

Table 5

	Components	Examples				
		6	7	8	9	10
Evaluation	Primer (Composition Example)	6	7	8	9	10
	Adhesive (Composition Example)	14	14	14	14	14
	Type of metal plate	Bonde	Bonde	Bonde	Bonde	Bonde
	Four-point bending strength (ordinary state)	201	252	263	272	261
	Four-point bending strength (after warm water resistance test)	194	249	257	270	255

Note: Unit of four-point bending strength: kgf/cm²

Table 6

	Components	Examples				
		11	12	13	14	15
Evaluation	Primer (Composition Example)	11	12	13	3	9
	Adhesive (Composition Example)	14	14	14	14	14
	Type of metal plate	Bonde	Bonde	Bonde	Galvanized sheet steel	Galvanized sheet steel
	Four-point bending strength (ordinary state)	250	227	271	223	269
	Four-point bending strength (after warm water resistance test)	247	216	265	217	266

Note: Unit of four-point bending strength: kgf/cm²

Table 7

	Components	Examples				
		16	17	18	19	20
Evaluation	Primer (Composition Example)	3	9	3	9	3
	Adhesive (Composition Example)	14	14	14	14	3
	Type of metal plate	Iron	Iron	Stainless steel	Stainless steel	Bonde
	Four-point bending strength (ordinary state)	219	258	231	273	209
	Four-point bending strength (after warm water resistance test)	217	254	228	271	202

Note: Unit of four-point bending strength: kgf/cm²

Table 8

	Components	Examples			
		21	22	23	24
Evaluation	Primer (Composition Example)	9	3	9	14
	Adhesive (Composition Example)	3	9	9	14
	Type of metal plate	Bonde	Bonde	Bonde	Bonde
	Four-point bending strength (ordinary state)	239	217	251	84
	Four-point bending strength (after warm water resistance test)	236	214	247	62

Note: Unit of four-point bending strength: kgf/cm²

Table 9

	Components	Comparative Examples				
		1	2	3	4	5
Evaluation	Primer (Composition Example)	Nil	Epoxy 1	Epoxy 3	Nil	Nil
	Adhesive (Composition Example)	Nil	Epoxy 2	Epoxy 4	3	9
	Type of metal plate	Nil	Bonde	Bonde	Bonde	Bonde
	Four-point bending strength (ordinary state)	60	180	173	101	137
	Four-point bending strength (after warm water resistance test)	62	70	68	79	93

Note: Unit of four-point bending strength: kgf/cm²

According to the present invention, it is possible to obtain a metal plate-bonded concrete which has high bond strength between dissimilar materials such as a metal plate and a concrete and which has water resistance whereby the bond strength will not be lowered even by moisture such as humidity. Accordingly, the bonding method for the metal plate-bonded concrete of the present invention is practically useful for reinforcing a concrete, and its effect is significant.

CLAIMS:

1. A metal plate-bonded concrete which comprises a concrete having its surface impregnated with a primer comprising (a) a (meth)acrylate having an ethylenically
5 unsaturated double bond in its molecule, (b) a polymerization initiator and (c) an activator, and a metal plate bonded to the concrete surface by an acrylic resin adhesive.
2. The metal plate-bonded concrete according to Claim 1,
10 wherein the (meth)acrylate (a) in the primer is a (meth)acrylate having an ethylenically unsaturated double bond which is not adjacent to a carbonyl group in its molecule.
3. The metal plate-bonded concrete according to Claim 1,
15 wherein the (meth)acrylate (a) in the primer is a monofunctional (meth)acrylate having an ethylenically unsaturated double bond in its molecule.
4. The metal plate-bonded concrete according to Claim 1,
wherein the (meth)acrylate (a) in the primer is a
20 polyfunctional (meth)acrylate having an ethylenically unsaturated double bond in its molecule.
5. The metal plate-bonded concrete according to any one of Claims 1 to 4, wherein the activator (c) in the primer contains a metal salt of an organic acid and/or a metal
25 organic chelate compound.
6. The metal plate-bonded concrete according to any one of Claims 1 to 5, wherein the primer contains (d) a



(meth)acrylate having no ethylenically unsaturated double bond in its molecule.

7. The metal plate-bonded concrete according to any one of Claims 1 to 6, wherein the surface of the metal plate
5 is made of zinc.

8. The metal plate-bonded concrete according to any one of Claims 1 to 6, wherein the surface of the metal plate is made of stainless steel.

9. A method for bonding a metal plate and a concrete,
10 which comprises impregnating a concrete surface with a primer comprising (a) a (meth)acrylate having an ethylenically unsaturated double bond in its molecule, (b) a polymerization initiator and (c) an activator, and then bonding a metal plate to the concrete surface by an
15 acrylic resin adhesive.

10. A primer which comprises (a) a (meth)acrylate having an ethylenically unsaturated double bond in its molecule, (b) a polymerization initiator and (c) an activator, and which is impregnated into a concrete surface prior to
20 bonding a metal plate to the concrete surface by an acrylic resin adhesive.

