

ADHESIVE COMPOSITION AND FILLER COMPOSITION
FOR CONCRETE

BACKGROUND OF THE INVENTION

5 Field of the Invention

This invention relates to an adhesive composition and a filler composition which are used for concrete. More particularly, it relates to an adhesive composition and a filler composition which are of a low-viscosity type and are highly safe, used not only for bonding artificial structures made of concrete, such as pipes and blocks, but also for stopping up cracks, gaps and so forth caused in such structures.

Related Background Art

15 With regard to adhesives and fillers for concrete, epoxy resins and urethane resins are conventionally in use because of their high performance.

For example, Japanese Patent Application Laid-Open No. 6-287972 and Japanese Patent Publication No. 20 3-79493 disclose examples of epoxy resins. The epoxy resins are commonly used in two-part adhesives comprised of a chief ingredient and a curing agent, and their curing is so greatly affected by environmental temperature that, in outdoor work in a low-temperature season, e.g., in winter, it usually takes few days 25 until adhesives cure completely.

Accordingly, urethane resins are used because of

This Sheet Has Been Replaced



their superior curability to epoxy resins, where two-part urethane adhesives comprised of a combination of polyols with urethane prepolymers terminated with isocyanate groups have better strength, curability and durability than one-part urethane adhesives using only urethane prepolymers terminated with isocyanate groups.

For example, Japanese Patent Application Laid-open No. 4-115061 discloses a repair method of repairing civil-engineering and constructional structures by filling their dry cracks with a mixture of a water-curable one-part polyurethane prepolymer and water glass. As the water-curable one-part polyurethane prepolymer, exemplified is a reaction product of a copolymer with tolylenediisocyanate; the copolymer being obtained by polymerization of ethylene glycol with ethylene oxide and propylene oxide.

However, in instances where urethane prepolymers terminated with isocyanate groups are commonly used, there is such a problem that the urethane prepolymers, terminated with isocyanate groups have a high viscosity not only in the one-part urethane adhesives but also in the two-part urethane adhesives. More specifically, any urethane prepolymers terminated with isocyanate groups can be obtained by the reaction of an organic polyisocyanate with a compound having active hydrogen groups as described later. In the resultant prepolymer, a urethane linkage produced as a result of

such polymerization reaction is contained. The urethane linkage, which is represented by "-NH-CO-O", tends to cause "hydrogen bond" intramolecularly and intermolecularly between the hydrogen atom and the oxygen atom, so that molecules themselves cohere to provide a high viscosity.

Such a high viscosity may not only make mixability and external appearance poor, but also make wettability and permeability poor to cause problems of faulty bonding and so forth. To solve such problems, a solvent or diluent having no active hydrogen capable of reacting with isocyanate groups may be added to decrease viscosity. In this case, however, since such an additive has no active hydrogen capable of reacting with isocyanate groups, the additive is by no means incorporated in the three-dimensional structure formed by the urethanation reaction of polyols with isocyanates and may dissolve out or disperse away with the passage of time, so that adhesive layers or filler layers may undergo volume shrinkage to cause problems of a decrease in strength and a decrease in durability. Thus, it has been impossible to meet the requirements of making viscosity low and retaining durability together.

SUMMARY OF THE INVENTION

The present invention was made taking account of

the above prior art. Accordingly, a object of the present invention is to make it possible to lower the viscosity of not only organic isocyanate compounds but also urethane prepolymers terminated with isocyanate groups and at the same time to prevent diluents from dissolving out or dispersing away with the passage of time. This object can be achieved by using a specific-component diluent having active hydrogen capable of reacting with isocyanate groups (hereinafter often "reactive diluent").

Another object of the present invention is to make it possible to form an inorganic-organic composite solid (solidified product) which has ever been difficult to form, and provide an adhesive and a filler which are used for concrete, and promise a great solidifying strength and also have superior stabilizing and reinforcing effect, durability, workability and economical advantages. This object can be achieved by a combination of i) an organic isocyanate composition obtained using the above reactive diluent with ii) an aqueous alkali silicate solution.

More specifically, the present invention provides an adhesive composition for concrete, which comprises;

- (A) an aqueous alkali silicate solution; and
- (B) a polyisocyanate composition having a viscosity of 400 mPa·s or less at 25°C; the polyisocyanate composition comprising a polyisocyanate

(B1) and a monoester compound (B2) which is derived from a monocarboxylic acid and a polyoxyalkylene alkyl ether and has a number-average molecular weight of 500 or less.

5 The present invention also provides a filler composition for concrete, which comprises;

 (A) an aqueous alkali silicate solution; and

 (B) a polyisocyanate composition having a viscosity of 400 mPa·s or less at 25°C; the
10 polyisocyanate composition comprising a polyisocyanate (B1) and a monoester compound (B2) which is derived from a monocarboxylic acid and a polyoxyalkylene alkyl ether and has a number-average molecular weight of 500 or less.

15 The above adhesive composition for concrete and filler composition for concrete may further contain (C) a catalyst and/or (D) a polyol.

 In the component-(B) polyisocyanate composition, the polyisocyanate (B1) comprises diphenylmethane
20 diisocyanate (b11) and a diphenylmethane-diisocyanate-type polycyclic condensate (b12), and the monoester compound (B2) is an adduct of a polyalkylene oxide with caprylic acid and 2-ethylhexanol or octanol.

25 DESCRIPTION OF THE PREFERRED EMBODIMENTS

 The adhesive composition for concrete and filler composition for concrete (hereinafter often "adhesive

composition" and "filler composition", respectively) of the present invention comprises the component-(A) aqueous alkali silicate solution, and component-(B) polyisocyanate composition having a viscosity of 400 mPa·s or less at 25°C; the polyisocyanate composition comprising a polyisocyanate (B1) and a monoester compound (B2) which is derived from a monocarboxylic acid and a polyoxyalkylene alkyl ether and has a number-average molecular weight of 500 or less. It may preferably further comprise the component-(C) catalyst and the component-(D) polyol.

The solidification reaction of the adhesive composition and filler composition of the present invention is too complicate to be elucidated. It is presumed that, when the component-(A) aqueous alkali silicate solution and the component-(B) polyisocyanate composition are mixed, silanol groups formed in the component (A) react with isocyanate groups contained in the component (B) to form a silicic acid anhydride/urethane composite, and at the same time, the component (B) reacts with water to generate carbon dioxide in the course of which a polymer made up through urea linkages and a silicic acid anhydride/urea cross-linked composite are formed and part of the carbon dioxide generated dissolves in the component (A) to effect gelation of alkali silicates contained in the component (A) to form a silicic acid anhydride gel. It

is also presumed that, where the component-(D) polyol is present, hydroxyl groups contained in the component-(D) polyol react with isocyanate groups contained in the component (B) to form urethane resin.

5 The silicic acid anhydride/urethane composite is made into an expanded solid by the carbon dioxide that is generated by the reaction of the component (B) with water and the water that is evaporated as water vapor by the heat of reaction which is generated when the
10 component (A) reacts with the component (B) or, where the component-(D) is contained, the component (A) and component (D) react with the component (B), enlarging its volume. The pressure of expansion at this stage makes the silicic acid anhydride/urethane composite
15 readily enter the gaps of artificial structures made of concrete. The adhesive composition and filler composition obtained in the present invention have a low viscosity, hence can more effectively permeate with ease into concrete to bring about an improvement in
20 bond strength and fill performance.

 The adhesive composition and filler composition of the present invention are described below concerning their components.

- (A) Aqueous Alkali Silicate Solution -

25 The component-(A) aqueous alkali silicate solution is, as mentioned previously, a component the silanol groups of which react chiefly with isocyanate groups of

the component (B) described later, to form a silicic acid anhydride/urethane composite.

The component-(A) aqueous alkali silicate solution may include, e.g., solutions composed chiefly of
5 potassium silicate and sodium silicate represented by $\text{Na}_2\text{O} \cdot x\text{SiO}_2$. The latter sodium silicate may include, e.g., those having an $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio of from 2:1 to 1:4. Stated specifically, it may include No.1 sodium silicate S2, No.2 sodium silicate N5, No.2
10 sodium silicate Q3 and No.2 sodium silicate T8 (all available from Toso Sangyo Co., Ltd.).

The component-(A) aqueous alkali silicate solution may also preferably be so regulated to have a solid content of from 10 to 70% by weight, and particularly
15 preferably from 20 to 50% by weight.

- (B) Polyisocyanate Composition -

The component-(B) polyisocyanate composition is a component which reacts with water to finally form a silicic acid anhydride gel in the manner as stated
20 above. The component (B) has a viscosity of 400 mPa·s or less at 25°C, and comprises a polyisocyanate (B1) and a monoester compound (B2) which is derived from a monocarboxylic acid and a polyoxyalkylene alkyl ether and has a number-average molecular weight of 500 or
25 less.

What is usable as the polyisocyanate (B1) may include, e.g., polyisocyanates alone or mixtures of two

or more of them, such as diphenylmethane diisocyanate (b11) (hereinafter often "MDI"), a diphenylmethane diisocyanate type polycyclic (or polynuclear) condensate (b12) (which is a diphenylmethane diisocyanate type polyisocyanate, and means a polyisocyanate having three or more aromatic nuclei; a compound named as a matter of convenience for defining the polyisocyanate used herein; not commercially available), a compound comprised of (b11) and (b12) (hereinafter "polymeric MDI", which is commercially available in the form of a product containing a dinuclear unit), liquid MDI (carbodiimide-modified MDI), tolylene diisocyanate, xylylene diisocyanate, trimethylene xylylene diisocyanate, isophorone diisocyanate, hexamethylene diisocyanate, naphthalene diisocyanate, hydrogenated diphenylmethane diisocyanate, and hydrogenated xylylene diisocyanate; and any of the above polyisocyanates to which a catalyst is added and made into dimmers or trimmers.

Besides the foregoing, also preferably usable as the polyisocyanate (B1) are isocyanate-group-containing urethane prepolymers obtained by reacting a monohydric alcohol or a polyol with any of the above polyisocyanates by a conventional process in such a way that, e.g., NCO groups and OH groups are in an equivalent weight ratio (NCO groups/OH groups) ranging from 1.5 to 500, and preferably from 2.0 to 400. The

monohydric alcohol and polyol usable here may include,
e.g., monohydric alcohols such as methanol, ethanol,
propanol, butanol, octanol and lauryl alcohol; diols
such as ethylene glycol, diethylene glycol, triethylene
5 glycol, 1,2-propanediol, 1,3-propanediol, dipropylene
glycol, 1,3-butanediol, 1,4-butanediol and
1,6-hexanediol; polyols such as glycerol,
trimethylolpropane and pentaerythritol; and besides,
those obtained by subjecting monoethanolamine,
10 diethanolamine, triethanolamine, diglycerol or
sorbitol, sucrose and diglycerol, used alone or in the
form of a mixture, to addition polymerization by a
known process, using an alkylene oxide such as ethylene
oxide, propylene oxide, butylene oxide or styrene oxide
15 alone or in combination.

The monohydric alcohol or polyol usable here may
preferably have an average molecular weight of from 76
to 10,000. If it has an average molecular weight
smaller than 76, the urethane prepolymer terminated
20 with isocyanate groups has a high urethane group
concentration and hence has a high viscosity, which may
not only make mixability and external appearance poor,
but also make wettability and permeability poor to
cause problems of faulty bonding and so forth. If on
25 the other hand it has an average molecular weight
larger than 10,000, it may have a poor compatibility
with the above isocyanate, so that any uniform urethane

prepolymer terminated with isocyanate groups may not be
obtained and also the resulting urethane prepolymer
terminated with isocyanate groups has a low urethane
group concentration to make adhesive layers or filler
5 layers have a low strength, undesirably.

The urethane prepolymer terminated with isocyanate
groups which is usable in the present invention may
preferably contain NCO groups in an amount of from 5 to
33% by weight, more preferably from 8 to 31% by weight,
10 and still more preferably from 10 to 30% by weight.

In order to make the adhesive composition or
filler composition well injectable, permeable and
wetable for any concrete artificial structures, the
component-(B) polyisocyanate composition used in the
15 present invention may preferably have a viscosity of
400 mPa·s or less, and more preferably from 30 to 300
mPa·s, at 25°C. If it has a viscosity higher than 400
mPa·s, the adhesive composition or filler composition
may poorly be injectable, permeable and wettable,
20 resulting in poor bond strength, fill performance and
durability, and meanwhile, resulting in low workability
especially in winter. If on the other hand it has a
viscosity lower than 30 mPa·s, the adhesive composition
or filler composition is liable to sag and can not
25 ensure its optimum quantity for bonding or filling,
resulting in poor bond strength or fill performance.

In order to obtain such component-(B)

polyisocyanate composition of a low-viscosity type of 400 mPa·s or less at 25°C, it is necessary to control the mixing proportion of the MDI and polymeric MDI which constitute the polyisocyanate composition. More specifically, these may preferably be in a proportion of MDI(b11)/polyisocyanate having three or more aromatic nuclei (b12) = 20/80 to 80/20 in weight ratio. If the MDI is too small, the polyisocyanate composition tends to have a high viscosity. If on the other hand the MDI is too much, precipitates tend to be formed because the MDI may crystallize during low-temperature storage.

As the MDI and the MDI in polymeric MDI, three types of isomers are available, i.e., 2,2'-MDI, 2,4'-MDI and 4,4'-MDI. In the present invention, any isomers of the MDI may be used.

In order to achieve the viscosity of 400 mPa·s or less at 25°C, it is necessary to use as the polyisocyanate (B1) not the polymeric MDI alone but the polymeric MDI and the MDI in combination. As the MDI, 4,4'-MDI is most readily available, and the resultant composition may more readily solidify with an increase in 4,4'-MDI (freezing point: about 39°C). Accordingly, in order to achieve low-temperature stability, it is preferable to use the 2,2'-MDI, the 2,4'-MDI and the polymeric MDI containing these MDIs.

Meanwhile, as a method for obtaining the

polyisocyanate composition of a low-viscosity type of
400 mPa·s or less at 25°C, an organic solvent such as
toluene, xylene, 1,1,1-trichloroethane, methylene
chloride or trichlorofluoromethane may also be used as
5 a diluent. Such a solvent, however, is volatile and
may become liberated after solidification to damage
environment. Accordingly, it is preferable not to use
such a solvent as far as possible.

In order to make the component (B) have a low
10 viscosity, a compound having no active hydrogen capable
of reacting with isocyanate groups may also be used as
a diluent, which includes diesters of aromatic or
aliphatic dibasic acids, acetates of mono- or
polyhydric alcohols, alkylene carbonates, ethers,
15 cyclic esters, acid anhydrides, and acrylates or
methacrylates of various types. In such a case, too,
it is preferable not to use any of these for the same
reasons as the above solvent.

More specifically, since in this case any of these
20 diluents have no active hydrogen capable of reacting
with isocyanate groups, the diluent is by no means
incorporated in the three-dimensional structure formed
by the urethanation reaction of polyols with
isocyanates and may dissolve out or disperse away with
25 the passage of time, so that adhesive layers or filler
layers may undergo volume shrinkage to cause problems
of a decrease in strength and a decrease in durability,

undesirably.

Accordingly, in the present invention, in addition to factors required in diluents such that they must have good stability and viscosity-reducing properties, studies have been made from the viewpoints of their compatibility with not only the component-(B) polyisocyanate composition but also the component-(A) aqueous alkali silicate solution, and the migration of diluent to the surfaces of adhesive layers and filler layers obtained by the adhesive composition and filler composition of the present invention. As the result, it has been discovered that the monoester compound (B2) which is derived from a monocarboxylic acid and a polyoxyalkylene alkyl ether and has a number-average molecular weight of 500 or less is preferable as a diluent.

This compound has very few active hydrogen groups, but is monofunctional, and may cause only a slight increase in viscosity even when it is allowed to react with the polyisocyanate contained in the component (B) and is made into the prepolymer terminated with isocyanate groups. In practical use, this compound is used in the form of a mixture with the polyisocyanate (B1).

As stated previously, while the component (A) and component (B) are mixed and in the course where silanol groups formed in the component (A) react with

isocyanate groups contained in the component (B) to form a silicic acid anhydride/urethane composite, the compound (B2), which contains a monocarboxylic component in its structure, is considered to have an affinity for the component (A). Also, while the component (B) reacts with water to generate carbon dioxide and a polymer made up through urea linkages and a silicic acid anhydride/urea cross-linked composite are formed, the component (B) is considered to form a composite with the component (A) and consequently form adhesive layers and filler layers to the surfaces of which the diluent may less migrate.

Even the monohydric polyols used to produce the urethane prepolymer terminated with isocyanate groups which is exemplified as one of the polyisocyanate (B1) has only one active-hydrogen group and hence has the like effect of reducing viscosity, but it does not have any effect as described above the reactive diluent of the present invention has, and is considered to be capable of forming only adhesive layers and filler layers inferior strength.

With regard to the monoester compound (B2), an acid component constituting its monoester may include, e.g., acetic acid, propionic acid, butyric acid, valerianic acid, caproic acid, caprylic acid, lauric acid and benzoic acid, as well as isomers of these.

An alcohol component constituting the monoester of

the compound (B2) may preferably include monohydric alcohols as exemplified by monools such as methanol, ethanol, propanol, butanol, octanol and lauryl alcohol, and isomers of these; alkanolamines such as

5 monoethanolamine, dimethylethanolamine, and isomers of these; and those obtained by subjecting diols such as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,3-propanediol, dipropylene glycol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol,

10 diethanolamine, triethanolamine and isomers of these, or polyols such as glycerol, trimethylolpropane, pentaerythritol and isomers of these, or glycerol, sorbitol, sucrose and isomers of these, used alone or in the form of a mixture, to addition polymerization by

15 a known process, using alkylene oxides such as ethylene oxide, propylene oxide, butylene oxide or styrene oxide alone or in combination along with the above monools or alkanolamines.

In the present invention, a monoester of caprylic acid and an alkylene oxide adduct of 2-ethylhexanol or

20 octanol is particularly preferred.

As the component-(B) polyisocyanate, a combination of a mixture of the MDI and the polymeric MDI, or an isocyanate-group-containing urethane polymer which is a

25 modified product of the mixture, with the above monoester is preferred in view of solidifying strength, safety and sanitation, and economical advantages.

The quantity of the component (B) to be mixed may differ depending on, e.g., the molar ratio of Na_2O and SiO_2 , and can not sweepingly be determined. Usually, it may preferably be so controlled that the mixing proportion of the component (A) and the component (B), component (A)/component (B), ranges from 10/100 to 100/10, and particularly from 20/100 to 100/20. If such a mixing proportion is smaller than the above lower limit, the adhesive composition and filler composition may require so high a cost as to be economically disadvantageous. If on the other hand it is larger than the above upper limit, the adhesive composition and filler composition may insufficiently solidify to remain uncured, or, even when cured, tend to be too low in hardness and too brittle to be put into practical use.

When the above diluent is used, it may commonly be mixed in an amount ranging from polyisocyanate (B1)/reactive diluent = 100/5 to 100/100.

20 - (C) Catalyst -

The component (C) catalyst used in the present invention includes those grouped roughly into metal-type catalysts and tertiary-amine-type catalysts, any of which may be used. It is a component acting as a catalyst for accelerating the reaction of the component-(A) aqueous alkali silicate solution and component-(D) polyol with the polyisocyanate (B1) to

effect curing. The component-(C) catalyst has a good compatibility with the component (A) aqueous alkali silicate solution and is readily removable by washing with water even when it adheres to the skin or clothes.

5 It also has a high catalytic activity.

As the metal-type catalysts, any catalysts may be used as long as they are metal compounds capable of exhibiting catalytic activity, including, e.g., esterified compounds, metal salts, acid derivatives,
10 oxides or chlorides of metals such as tin, zinc, calcium and titanium. As specific examples, they may include dibutyltin dilaurate, dioctyltin dilaurate, tin octylate, zinc octylate, calcium naphthenate, tetrabutyl titanate, tin oxide, tin chloride and
15 magnesium chloride.

As for the amine-type catalysts, they may include, as specific examples, catalysts such as triethylamine, triethylene diamine, N-methylmorpholine, N-methylimidazole, 1-methylimidazole, 1-ethylimidazole,
20 1-propylimidazole, 1-cyanoimidazole, 1-cyanomethylimidazole, 1,2-dimethylimidazole, 1,4-dimethylimidazole, 1-methyl-2-ethylimidazole, 1-methyl-4-ethylimidazole, 1-ethyl-2-methylimidazole, 1-ethyl-4-methylimidazole, pyridine, and α -picoline.

25 Amine type catalysts having active hydrogen capable of reacting with the component-(B) polyisocyanate composition also include

monoethanolamine, diethanolamine, triethanolamine,
N,N,N'-trimethylaminoethylethanolamine, and
N,N,N',N'-tetramethylhydroxypropylenediamine, which can
be mixed with the component (B).

5 In the present invention, in addition to the above
catalyst, coupling agents of various types, foaming
agents of various types, and also various additives
such as a surface-active agent, a dispersant, a
thickening agent, an antioxidant and a
10 heat-resistance-providing agent may be added, any of
which, however, should be limited to those which do not
cause any soil pollution at all events.

 The component-(A) aqueous alkali silicate solution
and the component-(C) catalyst may preferably be mixed
15 in an amount of from (A)/(C) = 100/0.1 to 100/20, and
particularly preferably from 100/0.5 to 100/15. If
such component-(C) catalyst is less than the above
lower limit, the adhesive composition or filler
composition may cure with difficulty and may cause so
20 insufficient solidification reaction as to make it
difficult to obtain solids (solidified products) having
the intended performance. If on the other hand it is
more than the above upper limit, it tends to cause so
rapid curing reaction as to make it difficult for the
25 components (A) and (B) to be mixed uniformly.

- (D) Polyol -

In the adhesive composition and filler composition

of the present invention, the component-(D) polyol may also be mixed in addition to the component-(A) aqueous alkali silicate solution, the component-(B) polyisocyanate composition and the component-(C) catalyst.

The component-(D) polyol used in the present invention may include, e.g., the polyols used in the polyisocyanate (B1) urethane prepolymer terminated with isocyanate groups, described previously. Any of these may be used alone or in the form of a mixture of two or more types. Also, these polyols may preferably have a number-average molecular weight of from 62 to 20,000, and particularly preferably from 76 to 10,000. The substantial average number of functional groups may preferably be 1 or more, and particularly preferably from 1 to 4.

The quantity of the component-(D) polyol to be mixed may differ depending on, e.g., the type of the component-(B) polyisocyanate composition and can not sweepingly be determined. Usually, it may preferably be so controlled that the mixing proportion of the component (B) to the component (D) ranges from 0.5 to 500, and particularly from 1 to 450, as a molar ratio of NCO groups in the component (B) and OH groups in the component (D) (NCO groups/OH groups). If the molar ratio of NCO groups to OH groups is less than the above lower limit, the adhesive layers and filler layers

obtained through the present invention tend to be too soft to be readily feasible for practical use. If on the other hand it is larger than the above upper limit, the adhesive layers and filler layers formed tend to be brittle.

- Other Additives -

For the purpose of controlling the dispersibility and reactivity between two phases of the component-(A) aqueous alkali silicate solution and the component-(B) polyisocyanate composition like the above, it is preferable to use a surface-active agent. The surface-active agent may include those obtained by polycondensation of a poly glycol ether containing an alkylene oxide such as ethylene oxide or propylene oxide with an organic compound having at least one active hydrogen. This organic compound having at least one active hydrogen may include alcohols, phenols, thiols, primary or secondary amines, and polyalkylene oxide derivatives of phenolic compounds having at least one alkyl substituent. The surface-active agent may previously be added to the component (A) and/or the component (B). Where, however, it is previously be added to the component-(A) aqueous alkali silicate solution, the mixture may foam when stirred to make it impossible to make measurement accurately. Accordingly, the surface-active agent may preferably be used after it has been mixed only in the component-(B)

polyisocyanate composition.

The surface-active agent may also include silicone-type surface-active agents, as exemplified by various siloxanepolyalkylene oxide block copolymers.

5 Stated specifically, it may include, e.g., L-5340, available from Nippon Unicar Co., Ltd., and B-8451 and B-8407, available from T. Goldschmidt Co. The surface-active agent may preferably be added in an amount of from 0.05 to 5% by weight based on the weight
10 of the polyisocyanate (B1).

In the adhesive composition and filler composition of the present invention, an inorganic filler such as cement, blast furnace slag, gypsum, calcium carbonate, clay, aluminum hydroxide, antimony trioxide, quick lime
15 (calcium oxide), slaked lime (calcium hydroxide) or bentonite, a diluent other than those described above, a leveling agent, a flame retardant, a silicone-type foam stabilizer, an age resistor, a heat-resistance-providing agent, an antioxidant, a
20 catalyst other than those described above and so forth may optionally further be mixed under appropriate control of mixing quantity.

In the present invention, various additives such as the above catalyst, the above surface-active agent
25 and the above various additives may be added, provided that they should be limited to those which do not adversely affect the human body and environment.

- Preparation of Compositions -

When the adhesive composition and filler composition of the present invention are prepared, there are no particular limitations on the order of mixing the components (A), (B) (C) and (D). Usually, these may preferably be used as a two-part preparation comprised of as part A a mixture of the component (A) and the component(s) (C) and/or (D) and as part B the component-(B) polyisocyanate composition, which is a mixture of the polyisocyanate (B1) and the monoester compound (B2).

The adhesive composition and filler composition comprised of the components (A) and (B) and further preferably the component(s) (C) and/or (D) can be used not only as an adhesive for concrete but also as a filler for stopping up cracks, gaps and so forth caused in artificial structures, to effect solidification or sealing. There are no particular limitations on methods for such bonding and filling to effect solidification or sealing, and any known methods may be employed. For example, a method is available in which a proportional-mixing pump which can control, e.g., the pour, pressure and mixing proportion of the components (A) and (B) is used, where as part A the mixture of the component (A) and preferably the component(s) (C) and/or (D) and as part B the mixture of the polyisocyanate (B1) and the monoester compound (B2) are

put in separate tanks, and these are applied to predetermined portions such as bonding portions and filling portions optionally using a static mixer to effect bonding or filling.

5 In the present invention, the sealing means to fill hollows or gaps with the adhesive composition and filler composition specified in the present invention to stop up any openings.

 The adhesive composition for concrete and filler
10 composition for concrete which are obtained by the present invention have a viscosity low enough to not only ensure a good operability but also attain high bond strength and fill performance because of their good permeability and wettability for gaps and cracks.
15 Also, since any diluent which may dissolve out with the passage of time is not used, the adhesive composition and filler composition can provide a superior durability and may less cause environmental pollution.

EXAMPLES

20 The adhesive composition for concrete and filler composition for concrete according to the present invention are described below in greater detail by giving preparation examples and working examples. The present invention is by no means limited to these
25 preparation examples and working examples.

Preparation of solutions A:

Using a mixer with a volume of 150 L, having a

stirrer, materials shown below were charged in the formulation shown in Table 1 and then mixed uniformly to prepare solutions A1 to A4. The materials were charged in quantities shown in Table 1.

5 Materials for synthesizing solutions A:

No.1 sodium silicate S2: An aqueous silicate solution (available from Toso Sangyo Co., Ltd.)

TEDA: Triethylene diamine (an amine-type catalyst)

DBTDL: Dibutyltin dilaurate (a metal-type catalyst)

10 DPG-200: Poly(oxypropylene)polyol

 Number-average molecular weight: 200

 Average number of functional groups: 2

DPG: Dipropylene glycol

 Synthesis of solutions B:

15 Using a reactor with a volume of 150 L, having a stirrer, a thermometer, a condenser and a nitrogen gas feed pipe, polyisocyanates B1 to B7 were synthesized.

 Starting-material isocyanate and starting-material polyol were charged in the formulation shown in Table 2, which were then heated to 80°C to carry out reaction for 3 hours, obtaining organic polyisocyanate compositions. Types of materials used are shown below, and their quantities and analytical values are shown in Table 2.

25 Materials for synthesizing solutions B:

MDI-1: MDI

 NCO content: 33.6%

$$2,2'\text{-MDI} + 2,4'\text{-MDI} = 0.1\%$$

MDI-2: MDI

NCO content: 33.6%

$$2,2'\text{-MDI} + 2,4'\text{-MDI} = 28\%$$

5 PMDI-1: Polymeric MDI

NCO content: 31.1%

MDI content in polymeric MDI: 42%

$$2,2'\text{-MDI} + 2,4'\text{-MDI in polymeric MDI} = 0.1\%$$

PMDI-2: Polymeric MDI

10 NCO content: 31.3%

MDI content in polymeric MDI: 36%

$$2,2'\text{-MDI} + 2,4'\text{-MDI in polymeric MDI} = 17\%$$

PEG-200: Poly(oxyethylene)polyol

Number-average molecular weight: 200

15 Average number of functional groups: 2

PPG-2000: Poly(oxypropylene)polyol

Number-average molecular weight: 2,000

Number of functional groups: 2

MPEG-1000: Polyethylene glycol monomethyl ether

20 Number-average molecular weight: 1,000

Number of functional groups: 1

Diluent A: Monoester of caprylic acid with ethylene
oxide adduct of 2-ethylhexanol

Diluent B: Monoester of propionic acid with ethylene
oxide adduct of 2-ethylhexanol.
25

Diluent C: Bis(2-ethylhexyl) adipate

B-8407: Silicone-type surface-active agent available

from T. Goldschmidt Co.

Examples 1 to 6 &

Comparative Examples 1 to 3

5 The solutions A and B were used in the combination shown in Tables 3 and 4, and bond strength under shear, fill performance, dissolution in water, and weatherability were tested by the following methods. Results obtained are shown in Tables 3 and 4.

10 As can be seen from the comparison of the various data shown in Tables 3 and 4, some data of some Comparative Examples show results comparable to Examples, but Comparative Examples show a low bond strength on the whole. In particular, in Comparative Example 2, any uniform adhesive layers were not applied
15 because of a high viscosity, resulting in a low bond strength. In Comparative Example 3, as can be seen from the test results of dissolution in water and weatherability, poor results were obtained because of dissolution of diluents.

20 Test methods:

(1) Bond strength under shear

Solutions A and solutions B were individually put together at 25°C in an amount of 100 g each, and mixed with stirring. Thereafter, a portion of each resultant
25 liquid in a fluid state was quickly applied to concrete blocks (length: 100 mm; width: 100 mm; thickness: 20 mm) at their surfaces having an area of 50 mm x 50 mm,

by means of a metal rod. Thereafter, these blocks were pressed from the top and bottom at about 5 MPa. Test samples were thus prepared. Then, their bond strength under shear was measured according to JIS K-6250 under conditions of 25°C and 60%RH.

(2) Fill performance

Solutions A and solutions B were individually put together at 25°C in an amount of 100 g for each, and mixed with stirring for 10 minutes by means of a metal rod. A portion of each resultant liquid was put to a concrete block (length: 200 mm; width: 200 mm; thickness: 40 mm) having a hollow of 100 mm long, 100 mm wide and 20 mm deep, so as to fill the hollow with the liquid. Immediately thereafter, a concrete block having the same shape but having no hollow was put thereon, and these blocks were pressed at about 5 MPa. Test samples were thus prepared. Then, after the lapse of 1 hour at 25°C, the blocks were put open to check how each hollow was filled with. A sample whose hollow was completely filled was judged "good"; and a sample whose hollow was partly not filled, "poor".

(3) Dissolution-in-water test

Solutions A and solutions B were individually put together, and each resultant liquid in a fluid state immediately thereafter was quickly put in a polyethylene cup holding therein 300 ml of water previously, observing how the liquid foamed in water.

In this observation, a case where the water in the polyethylene cup became turbid in white was judged "poor"; and a case where it was kept clear, "good".

(4) Weatherability

5 Samples into hollows of which the liquid was poured, used in the test on "fill performance", were left standing conditions of 50°C, and the surface state of each resultant solid (solidified matter) was observed. A sample to the surface of which any liquid
10 substance oozed out was judged "poor; and a sample showing no change, "good".

Table 1

	Solution-A Preparation Example			
	1	2	3	4
Aqueous silicate solution: (kg)				
No.1 sodium silicate S2	100	100	100	100
Catalyst: (kg)				
TEDA	3.0	3.0	3.4	
DBTDL				3.0
Polyol: (kg)				
PPG200		5.0	5.0	5.0
DPG			0.6	
Solutions A:	A1	A2	A3	A4

Table 2

	Solution-B Preparation Example						
	1	2	3	4	5	6	7
Polyisocyanate: (kg)							
MDI-1	200						
MDI-2		333					
PMDI-1	800			1,000	1,000		1,000
PMDI-2		667	1,000			1,000	
Polyol: (kg)							
PEG-200			50	90		90	
PPG-2000	10						
MPEG-1000		20					
Diluent: (kg)							
Diluent A	50			510			
Diluent B		280	150				
Diluent C							400
Surface-active agent: (kg)							
B-8407	1.0	1.0	1.0				1.0
NCO content: (%)	29.8	24.6	24.3	17.1	31.1	25.3	22.2
Viscosity at 25°C: (mPa·s)	120	50	70	200	180	540	80
Solutions B:	B1	B2	B3	B4	B5	B6	B7

Table 3

	Example					
	1	2	3	4	5	6
Solutions A:	A1	A2	A3	A4	A4	A1
Solutions B:	B1	B1	B1	B2	B3	B4
Bond strength under shear: (N/mm ²)	27	31	33	32	31	29
Fill performance:	good	good	good	good	good	good
Dissolution in water:	good	good	good	good	good	good
Weatherability:	good	good	good	good	good	good

Table 4

	Comparative Example		
	1	2	3
Solutions A:	A4	A4	A4
Solutions B:	B5	B6	B7
Bond strength under shear: (N/mm ²)	15	8	6
Fill performance:	poor	good	good
Dissolution in water:	good	good	poor
Weatherability:	good	good	poor



WHAT IS CLAIMED IS:

1. An adhesive composition for concrete, which comprises:

(A) an aqueous alkali silicate solution; and

5 (B) a polyisocyanate composition having a viscosity of 400 mPa's or less at 25°C; the polyisocyanate composition comprising a polyisocyanate (B1) and a monoester compound (B2) which is derived from a monocarboxylic acid and a polyoxyalkylene alkyl
10 ether and has a number-average molecular weight of 500 or less.

2. The adhesive composition according to claim 1, which further comprises at least one of (C) a catalyst
15 and (D) a polyol.

3. The adhesive composition according to claim 1 or 2, wherein the polyisocyanate (B1) comprises diphenylmethane diisocyanate (b11) and a
20 diphenylmethane-diisocyanate-type polycyclic condensate (b12), and the monoester compound (B2) is derived from a caprylic acid and an alkylene oxide adduct of 2-ethylhexanol or octanol.

25 4. A filler composition for concrete, which comprises:

(A) an aqueous alkali silicate solution; and



(B) a polyisocyanate composition having a viscosity of 400 mPa·s or less at 25°C; the polyisocyanate composition comprising a polyisocyanate (B1) and a monoester compound (B2) which is derived
5 from a monocarboxylic acid and a polyoxyalkylene alkyl ether and has a number-average molecular weight of 500 or less.

5. The filler composition according to claim 4,
10 which further comprises at least one of (C) a catalyst and (D) a polyol.

6. The filler composition according to claim 4 or 5, wherein the polyisocyanate (B1) comprises
15 diphenylmethane diisocyanate (b11) and a diphenylmethane-diisocyanate-type polycyclic condensate (b12), and the monoester compound (B2) is derived from a caprylic acid and an alkylene oxide adduct of 2-ethylhexanol or octanol.