



(86) Date de dépôt PCT/PCT Filing Date: 2012/10/24  
(87) Date publication PCT/PCT Publication Date: 2013/05/02  
(45) Date de délivrance/Issue Date: 2019/11/26  
(85) Entrée phase nationale/National Entry: 2014/04/15  
(86) N° demande PCT/PCT Application No.: IB 2012/055842  
(87) N° publication PCT/PCT Publication No.: 2013/061255  
(30) Priorité/Priority: 2011/10/24 (ESP201131708)

(51) Cl.Int./Int.Cl. *C09J 163/00* (2006.01)  
(72) Inventeurs/Inventors:  
PARELLADA LLOBET, JORGE, ES;  
ARBUSA AMOROS, JORDI, ES;  
BORROS GOMEZ, SALVADOR, ES  
(73) Propriétaires/Owners:  
PJM PUJADAS, S.A., ES;  
INSTITUT QUIMIC DE SARRIA CETS FUNDACIO  
PRIVADA, ES  
(74) Agent: MACRAE & CO.

(54) Titre : COMPOSITION D'ADHESIF  
(54) Title: ADHESIVE COMPOSITION

(57) **Abrégé/Abstract:**

The present invention relates to an adhesive composition comprising component A which comprises bisphenol A resin; a hydrophilic solvent, acetone or ethanol or mixtures thereof; and silica gel (SiO<sub>2</sub>) or alumina (Al<sub>2</sub>O<sub>3</sub>) and component B which comprises aliphatic or aromatic polyamines, preferably polyamidoamines; polythiol; a combination of primary and tertiary amines, preferably 1-(2-aminoethyl)piperazine and ethylenediamine; optionally a hydrophilic solvent and optionally silica (SiO<sub>2</sub>) or alumina (Al<sub>2</sub>O<sub>3</sub>) gel. Said composition has the advantage that it cures, in addition to under dry conditions, in the presence of water or humidity in 30 minutes or less and is flexible. The invention also relates to a process for preparing the adhesive composition.

## **ABSTRACT**

The present invention relates to an adhesive composition comprising component A which comprises bisphenol A resin; a hydrophilic solvent, acetone or ethanol or mixtures thereof; and silica gel ( $\text{SiO}_2$ ) or alumina ( $\text{Al}_2\text{O}_3$ ) and component B which comprises aliphatic or aromatic polyamines, preferably polyamidoamines; polythiol; a combination of primary and tertiary amines, preferably 1-(2-aminoethyl)piperazine and ethylenediamine; optionally a hydrophilic solvent and optionally silica ( $\text{SiO}_2$ ) or alumina ( $\text{Al}_2\text{O}_3$ ) gel. Said composition has the advantage that it cures, in addition to under dry conditions, in the presence of water or humidity in 30 minutes or less and is flexible. The invention also relates to a process for preparing the adhesive composition.

## **ADHESIVE COMPOSITION**

### **FIELD OF THE INVENTION**

5 The present invention relates to the field of adhesives.

### **BACKGROUND OF THE INVENTION**

10 The importance of adhesives in the modern world is well known, both on an industrial and professional level. They are used in a multitude of manufacturing processes to perform bonds, for example, in sectors such as graphic arts, transformation of paper and cardboard, containers and packaging, furniture and wood, the car industry, etc. They are also very important in the installation or bonding of materials, especially in construction (adhesives for pavements and coverings such as carpets, PVC, linoleum,...).  
15 Even on a domestic or children's level, their use is fairly widespread. Obviously due to this great variety of fields of application, their composition is quite variable. In this way, we can have adhesives of solid, liquid, acrylic types, cyanoacrylates, epoxy, etc.

On a technical level, an adhesive is defined as a mixture of substances that serves to keep two supports bonded together by surface interactions. These interactions may be of physical or chemical type  
20 (chemical bonds). The bonding mechanism of an adhesive is based on a balance of two forces:

Adhesive force ( $F_a$ ): the force that must be exerted to separate the adhesive from the surface.

Cohesive force ( $F_c$ ): the force that must be exerted to break the internal structure of the adhesive.

25 A good adhesive is characterized in that it causes ruptures of cohesive type, i.e. the adhesive must break before separating from the support. In some cases it may be of interest that ruptures of the support appear (for structural adhesives).

A cohesive rupture is characterized as it appears in a system wherein  $F_c < F_a$ .

30 This can be achieved by adhesives with low  $F_c$ : low resistance bonds or by systems providing very high  $F_a$  (incorporating adherence promoters, for example).

35 However, one of the current difficulties is finding adhesives capable of curing when the place where they are applied is in contact with high humidity or directly in contact with water and that, furthermore, said curing is performed in the shortest possible period of time. This is of great importance when the working conditions are usually surrounded by an aqueous medium, such as, for example, in a boat, in the repair of submerged pipes, applications in plumbing, nautical construction and repairs, or, in general, any utensil which, due to its characteristics, must be in continuous contact with water and it is required that the

adhesive acts as fast as possible.

Currently, there are adhesive compositions that are used for curing in said aqueous conditions but their efficacy is far from optimum. Examples of said commercial products are the Marine Adhesive fast cure  
5 5200™ from 3 M™, or Hysol U-05FL™ from Loctite™.

Document JP200033633 discloses a water-resistant adhesive comprising two components A and B, where component A is an epoxy resin composition modified with urethane, bisphenol A resin and acrylic particles and component B is a polyamidoamine.  
10

Document JP 60023467 relates to an adhesive with excellent water resistance properties and is composed of formaldehyde, bisphenol A-type epoxy resin and optionally an epoxy resin hardener such as, for example, compounds with amino groups.

15 Document JP59191713 discloses the use of an epoxy resin mixture derived from bisphenol A and polyamidoamine in a composition with iron oxide and a fibrous material to obtain a material with great adhesiveness to metals, wood and good resistance in water.

The present inventors have surprisingly obtained an adhesive composition with the capacity of curing, in  
20 addition to under dry conditions, under humid conditions or submerged in water (being this water, for example, pure water, fresh water, salt water, sea water, ocean water, contaminated water, and, in general, solutions where the major solvent is water) in a period of time of 30 min as much, with the capacity of bonding any type of material, whether in dry or humid conditions or submerged in water, and additionally having a flexible behaviour once cured which makes it especially indicated for demands  
25 where a flexible bond is required and with variability in form. All these properties are kept even at temperatures around 5°C.

None of the previously mentioned documents disclose an adhesive composition as disclosed in the present invention having at the same time all the above disclosed properties.  
30

Consequently, a first object of the present invention is to achieve an adhesive composition which has the capacity to cure, in addition to under dry conditions, in an aqueous medium (i.e. submerged in water, considering that this water can be, for example, pure water, fresh water, salt water, sea water, ocean water, contaminated water, and, in general, solutions where the major solvent is water) or with humidity in  
35 the shortest possible time (30 min as much) and also be flexible, this last parameter being easily controllable by the modification of the adhesive composition.

Another object of the present invention is to develop a process whereby the adhesive composition described herein is obtained.  
40

Another further object of the present invention is to provide the use of the adhesive composition of the present invention to bond any type of surface in any environmental condition, whether with water or without it.

## 5 BRIEF DESCRIPTION OF THE INVENTION

The present invention firstly relates to an adhesive composition comprising a component A and a component B, wherein said component A comprises bisphenol A resin; a hydrophilic solvent, preferably acetone or ethanol or mixtures thereof; and silica ( $\text{SiO}_2$ ) or alumina ( $\text{Al}_2\text{O}_3$ ) gel and said component B  
10 comprises aliphatic or aromatic polyamines, preferably polyamidoamines; polythiol; a combination of primary and tertiary amines, preferably 1-(2-aminoethyl)piperazine and ethylenediamine; optionally a hydrophilic solvent and optionally silica ( $\text{SiO}_2$ ) or alumina ( $\text{Al}_2\text{O}_3$ ) gel. Said composition has the advantage that it cures, in addition to under dry conditions, in the presence of water or humidity or submerged in  
15 water, considering that this water can be, for example, pure water, fresh water, salt water, sea water, ocean water, contaminated water, and, in general, solutions where the major solvent is water, in a time of 30 minutes as much and is flexible. Additionally, the degree of flexibility can be easily controlled by the modification of the adhesive composition.

The present invention also relates to a process for obtaining said adhesive composition.

20 Finally, the present invention also relates to the use of the adhesive composition of the present invention for the bonding of any type of material in a medium with the presence of water and without it, and of materials where a flexible behaviour is necessary.

## 25 DETAILED DESCRIPTION OF THE INVENTION

The present invention relates in a first aspect to an adhesive composition comprising a component A and a component B, wherein said component A comprises:

- bisphenol A resin;
- 30 - a hydrophilic solvent, preferably acetone or ethanol or mixtures thereof; and
- silica ( $\text{SiO}_2$ ) or alumina ( $\text{Al}_2\text{O}_3$ ) gel

and said component B comprises:

- aliphatic or aromatic polyamines, preferably polyamidoamines;
- polythiol;
- 35 - a combination of primary and tertiary amines, preferably 1-(2-aminoethyl)piperazine and ethylenediamine;
- optionally a hydrophilic solvent; and
- optionally silica ( $\text{SiO}_2$ ) or alumina ( $\text{Al}_2\text{O}_3$ ) gel.

40 As indicated above, the component hydrophilic solvent can be optionally present in the formulation of

component B.

As indicated above, the component silica ( $\text{SiO}_2$ ) or alumina ( $\text{Al}_2\text{O}_3$ ) gel can be optionally present in the formulation of component B.

As indicated above, the component hydrophilic solvent and the component silica ( $\text{SiO}_2$ ) or alumina ( $\text{Al}_2\text{O}_3$ ) gel can be both optionally present together in the formulation of component B.

Said composition has the advantage that it cures, in addition to under dry conditions, in the presence of humidity or submerged in water in a time of 30 minutes as much and is flexible.

By "submerged in water" is understood in the present invention that the components to be cured are in contact with water, being this water pure water, fresh water, salt water, sea water, ocean water, contaminated water, and, in general, solutions where the major solvent is water.

The bisphenol A resin used in the present invention preferably has a number average molecular weight lower than 700 ( $M_n < 700$ ).

Throughout the present invention, previously and subsequently, "flexibility" is understood when applied to a material or that a material is "flexible" a material which has a high deformation in the elastic limit.

In the present invention "hydrophilic solvent" is understood as any solvent which has the capacity of being partially or totally dissolved in water. Preferably, acetone or ethanol is used. This component provides the capacity of curing under water submerging conditions without altering the curing rate, the flexibility and the adhesiveness capacity.

In a preferred embodiment, each compound of component A has the following concentrations: bisphenol A resin between 35 and 45% by weight, hydrophilic solvent between 10 and 15% by weight and  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  between 10 and 15% by weight over the total composition and each compound of component B has the following concentrations: aliphatic or aromatic polyamines between 30 and 40% by weight, polythiol between 3 and 4.5% by weight, combination of primary and tertiary amines between 0.5 and 2.5% by weight over the total composition.

The polythiol used in the present invention is preferably a polythiol of high molecular weight. The greater this molecular weight, the greater flexibility will be achieved in the final adhesive composition.

In a particular embodiment, this composition additionally has a great flexibility which has experimentally been demonstrated that it corresponds to a deformation between 3 and 5% on applying a load between 2.5 and 9 N, respectively.

In a particular embodiment, the present composition may further comprise, whether with component A or with component B, one or more additional components selected from the group consisting of: at least one

ultraviolet light stabilizer (for example, tinuvin type), metal powder, optionally nanometric, to achieve an adhesive conductor, at least one antifungal agent such as, for example, copper salts, preferably in 0.5% by weight, at least one antioxidant (for example, BHT type), at least one water-miscible organic solvent (for example, ethylene glycols, alcohols), at least one viscosity-regulator agent and at least one  
5 thixotropic agent, or mixtures thereof.

The adhesive composition of the present invention, according to any of the embodiments disclosed herein, has the following properties:

- Curing under dry or humid conditions or submerged in water in a time of 30 minutes as much
- 10 - Great flexibility once cured
- Capacity of bonding any type of material, whether in dry or humid conditions or submerged in water
- Invariability of the above properties at low temperatures (even at temperatures around 5°C)

15 In a second aspect, the present invention relates to a process for obtaining an adhesive composition disclosed in the present invention according to any of the previous embodiments comprising the initial mixture of the components of B, also optionally with the components of A with the exception of the bisphenol A resin, and the subsequent mixture of the bisphenol A resin with the initial mixture if it already contains the remaining components of A or with the initial mixture and the remaining components of A if  
20 the initial mixture of the components of B was not mixed with the components of A.

The objective of making the mixture separately of the bisphenol A resin and the components of B is to prevent the start of the curing reaction, being it possible to add both the silica or alumina gel and the hydrophilic solvent in both components, in order to adjust to a suitable stoichiometric proportion  
25 depending on the final properties desired for the adhesive.

A third aspect of the present invention relates to the use of the adhesive composition disclosed in the present invention according to any of the previous embodiments wherein the materials to be bonded by said adhesive composition are for example, but without being limited thereto, wood, metals, ceramics,  
30 polymeric or materials composed with mixtures of said materials.

In a particular embodiment, said materials have water in any of their physical states on their surface.

In another particular embodiment, said materials have no water in any of their physical states on their  
35 surface.

In another particular embodiment, said materials are submerged in water, being this water, pure water, fresh water, salt water, sea water, ocean water, contaminated water, and, in general, solutions where the major solvent is water.

In a preferred embodiment, the adhesive composition disclosed in the present invention according to any of the previous embodiments is used to bond materials, such as, but without being limited thereto, wood, metals, ceramics, polymeric or materials composed with mixtures of said materials, wherein the bonding zone between the composition and the surface of the material requires a flexible behaviour or with mobility.

### **Examples**

The following examples of compositions are provided to explain and illustrate the present invention and are not intended to be limiting thereof. All the percentages relate to % by weight.

For a faster reading, the following abbreviations have been used:

Bisphenol A Resin ( $W_n < 700$ ) = BPAR

High molecular weight polythiol = DAP

15 1-(2-Aminoethyl)piperazine = APZ

Ethylenediamine = EDA

#### **Composition 1:**

4 parts of BPAR (41%)  
20 3 parts of Polyamidoamine (31%)  
0.3 parts of DAP (3%)  
0.1 parts of APZ (1%)  
0.1 parts of EDA (1%)  
1.125 parts of Acetone (11.5%)  
25 1.125 parts of silica gel (11.5%)

This composition has a curing time of 25 minutes. The final appearance of the adhesive is flexible, it has an excellent behaviour against curing in the presence of or submerging in water (pure water, fresh water, salt water, sea water, ocean water, contaminated water, and, in general, solutions where the major solvent is water). The same properties were obtained at 10°C, room temperature and 45°C.

#### **Composition 2:**

4 parts of BPAR (41%)  
3 parts of Polyamidoamine (31%)  
35 0.4 parts of DAP (4%)  
0.05 parts of APZ (0.5%)  
0.05 parts of EDA (0.5%)  
1.125 parts of Acetone (11.5%)  
1.125 parts of silica gel (11.5%)  
40 This composition has a curing time of 30 minutes. The final appearance of the adhesive is very flexible

and has a very good behaviour against curing in the presence of or submerging in water (pure water, fresh water, salt water, sea water, ocean water, contaminated water, and, in general, solutions where the major solvent is water). The same properties were obtained at 10°C, room temperature and 45°C.

5 **Comparative composition 3:**

4 parts of BPAR (41%)

3 parts of Polyamidoamine (31%)

0.5 parts of DAP (5%)

1.125 parts of Acetone (11.5%)

10 1.125 parts of silica gel (11.5%)

This composition has a curing time close to 80 minutes.

**Comparative composition 4:**

15 4 parts of BPAR (41%)

3 parts of Polyamidoamine (31%)

0.25 parts of APZ (2.5%)

0.25 parts of EDA (2.5%)

1.125 parts of Acetone (11.5%)

20 1.125 parts of silica gel (11.5%)

**Comparative composition 5:**

4 parts of BPAR (53,34%)

3 parts of Polyamidoamine (40%)

25 0.3 parts of DAP (4%)

0.1 parts of APZ (1,33%)

0.1 parts of EDA (1,33%)

30 This composition has a curing time of 20 minutes, however it does not have the capacity to cure correctly in the presence of water.

## CLAIMS

1. An adhesive composition comprising a component A and a component B, wherein said component A comprises:

- bisphenol A resin;
- a hydrophilic solvent; and
- silica (SiO<sub>2</sub>) or alumina (Al<sub>2</sub>O<sub>3</sub>) gel;

and said component B comprises:

- aliphatic or aromatic polyamines;
- polythiol;
- a combination of primary and tertiary amines;
- optionally a hydrophilic solvent, and
- optionally silica (SiO<sub>2</sub>) or alumina (Al<sub>2</sub>O<sub>3</sub>) gel,

wherein the hydrophilic solvent is acetone, ethanol or a mixture thereof;

wherein each component of component A has the following concentrations: bisphenol A resin between 35 and 45% by weight, hydrophilic solvent between 10 and 15% by weight and SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> between 10 and 15% by weight, over the total composition; and

wherein each component of component B has the following concentrations: aliphatic or aromatic polyamines between 30 and 40% by weight, polythiol between 3 and 4.5% by weight, combination of primary and tertiary amines between 0.5 and 2.5% by weight, over the total composition.

2. The composition as defined in claim 1, wherein the combination of primary and tertiary amines is 1-(2-aminoethyl)piperazine and ethylenediamine.

3. The composition as defined in claim 1, wherein the aliphatic or aromatic polyamines are polyamidoamines.

4. The composition as defined in any one of claims 1-3, further comprising one or more additional components selected from the group consisting of: at least one ultraviolet light stabilizer, metal powder, at least one antioxidant, at least one antifungal agent, at least one water-miscible organic solvent, at least one viscosity-regulator agent, at least one thixotropic agent, and mixtures thereof.

5. A process for obtaining the composition according to any one of claims 1 to 4, comprising:

- i) preparing a mixture of the components of A except for the bisphenol A resin;
- ii) preparing a mixture of the components of B; and
- iii) mixing the bisphenol A resin with the mixture prepared in step ii) and with the

mixture prepared in step i).

6. A process for obtaining the composition according to any one of claims 1 to 4, comprising:
  - i) preparing a mixture of the components of B and the components of A except for the bisphenol A resin; and
  - ii) mixing the mixture prepared in step i) with the bisphenol A resin.
  
7. Use of the composition defined in any one of claims 1 to 4 as an adhesive to bond materials, wherein the materials to be bonded are wood, metals, ceramics, polymerics or materials composed of mixtures of said materials.
  
8. The use according to claim 7, wherein at least one surface of the materials has water in any physical state on said one or more surfaces.
  
9. The use according to claim 7, wherein the materials are bonded in a bonding zone between the composition and the surface of the material and wherein the bonding zone requires a flexible behaviour or movement.