PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :		(11) International Publication Number:
C09J 115/02, 123/08, 133/06	A1	WO 93/18105
		(43) International Publication Date: 16 September 1993 (16.09.93)

(21) International Application Number: PCT/PL93/00002

(22) International Filing Date: 5 March 1993 (05.03.93)

(30) Priority data:
P-293774 10 March 1992 (10.03.92) PL

(71) Applicant: INSTYTUT CHEMII PRZEMYSLOWEJ [PL/PL]; ul. Rydygiera 8, 01-793 Warszawa (PL).

(72) Inventors: PENCZEK, Piotr ; ul. Corazziego 4 m.25, 00-087 Warszawa (PL). STANIAK, Henryk ; ul. Burgaska 6 m.92, 02-758 Warszawa (PL).

(81) Designated States: CZ, RU, UA, European patent (AT, BE, DE, ES, FR, GB, IT, NL, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD FOR MAKING AQUEOUS DISPERSION-BASED ADHESIVE

(57) Abstract

This invention relates to a method of making a water resistant, aqueous dispersion-based adhesive. The adhesive is recommended mainly for bonding plastic flooring to concrete substrate. In the method according to the invention, 5-50 weight parts of epoxide resin or a modified epoxide resin are introduced to an aqueous dispersion of ethylene vinyl acetate copolymer, or of an acrylic ester copolymer, or of a chloroprene copolymer. That amount is related to 100 weight parts of said copolymers having a glass transition temperature below -5 °C. Separately a liquid polyaminoamide curing agent is emulsified in water or in an aqueous dispersion of same copolymer. While using 20-100 weight parts of polyaminoamide per 100 weight parts of epoxide resin and mixing both components of the adhesive, it is applied to the substrates to be bonded.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SK	Slovak Republic
CI	Côte d'Ivoire	KZ	Kazakhstan	SN	Senegal
CM	Cameroon	LI	Liechtenstein	SU	Soviet Union
CS	Czechoslovakia	LK	Sri Lanka	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	UA	Ukraine
DK	Denmark	MG	Madagascar	US	United States of America
ES	Spain	ML	Mali	VN	Viet Nam
FI	Finland	MN	Mongolia		

METHOD FOR MAKING AQUEOUS DISPERSION-BASED ADHESIVE

This invention relates to a method of making a water resistant, aqueous disperion-based adhesive. The said adhesive is a two-component one and contains high molecular weight copolymers as its main component. The adhesive is recommended mainly for bonding plastic flooring to concrete substrate.

The bonds obtained using aqueous dispersion-based adhesives known in the art have unsatisfactory resistance to long-term exposure to water. Moreover, the known adhesives cannot be used for bonding plastic flooring to wet, freshly prepared concrete. An example of such known adhesive is an aqueous dispersion-based adhesive manufactured by BASF. Main component of BASF adhesive is a product of acrylic esters copolymerization sold under a trade name Acronal V-271. This adhesive contains also: a filler, an emulsifier, large amount of resin (in toluene solution) and other additives. This adhesive has good bond strength when bonding plasticized PVC flooring, but its resistance to long-term exposure to water is limited.

Polychloroprene latex-based adhesives are widely used for bonding a variety of materials. It became possible because many different natural and synthetic resins, other lattexes and aqueous dispersions or emulsions of various

polymers as well as starch, proteins and other additives usually applied to modify the processing and application properties of the adhesive have been introduced to the basic adhesive binder--a chloroprene copolymer. Coalescing agents and sometimes solvents have been also used to get a continuous adhesive film.

Low glass transition temperature of chloroprene copolymer is of great importance to ensure a good tack of the adhesive. However, it is desirable to add resins of appropriate softening temperature in order to get good coalescence and good properties of the adhesive bonds. One of the few disadvantages of polychloroprene rubber-based adhesives is low initial resistance to water. Water resistance of the adhesive bonds made using aqueous dispersions of ethylene vinyl acetate copolymers is also unsatisfactory.

It is, however, known in the art that aqueous dispersions of acrylic copolymers containing epoxide, imine or amide groups in the molecule are used in coatings to improve their weathering characteristics and thus also water resistance.

In European Patent 0172460, a two-component aqueous dispersion used in coatings is described. First component is epoxide groups containing acrylic copolymer (product of copolymerization of acrylic esters, mainly methyl acrylate and methyl methacrylate, styrene and glicydyl methacrylate), and second component is an ether

bond containing high molecular weight aliphatic diamine of molecular weight below 5000.

In U. S. Patent 3,945,963, an aqueous emulsion-based solvent-containing coating composition is described. The first component is an imine group containing acrylic copolymer (product of copolymerization of acrylic acid esters, methacrylic acid esters, unsaturated monomers, e.g. styrene, acrylonitrile, and unsaturated hydrocarbons with unsaturated carboxylic acids being then partially or totally reacted with alkyleneimine. The second component is water-dispersed solid epoxide resin of very high molecular weight (40,000 to 60,000).

U. S. Patent 4,289,674 teaches about aqueous dispersions obtained by combining an amide group containing aqueous dispersions of acrylic copolymers (obtained by solution copolymerization of N-methoxyacrylamide, or N-methoxymethacrylamide, unsaturated carboxylic acids and a vinyl monomer) with high molecular weight, solid epoxide resin dispersed in water.

Room temperature-crosslinkable coatings or adhesive films can be obtained from such known products composed of solid constituents only when they contain organic solvents.

The objective of this invention was to develop a process of manufacturing solventless, water-resistant adhesives that can be applied for bonding substrates soaked with water and that would yield adhesive bonds resistant to long-term exposure to water. The additional objective of

this invention is to reach this goal by using aqueous dispersions of standard, simple copolymers that would not contain any reactive functional groups, small amount of carboxylic groups that would help in getting stable aqueous dispersion being an exception.

It has been found unexpectedly that it is possible to make adhesives which can be applied for water-soaked substrates and are characterized by a very good resistance of the adhesive bond to long-term exposure to water, by blending chloroprene copolymer, acrylic ester copolymer, or ethylene-vinyl acetate copolymer, said copolymers not containing reactive functional groups except optionally carboxylic groups and having glass transition temperature below -5°, with liquid epoxide resin, when using as a curing agent a low molecular weight polyaminoamide being separately emulsified in aqueous dispersion of the same copolymer or in water, said curing agent being added to the first component that contains said copolymer and said epoxide resin not later than 8 hours before the adhesive is used.

Amount of polyaminoamide is 20 to 100 pph (parts by weight per 100 parts by weight) of epoxide resin, preferably 40 to 70 pph of epoxide resin. Amount of epoxide resin is 5 to 50 pph of polymer dispersion, preferably 10 to 30 pph of polymer dispersion. It is preferred to use the epoxide resin being previously modified by addition of either an aliphatic amine or a cycloaliphatic amine bearing primary or secondary amine group or by addition of a monocarboxylic acid, said acid being preferably lactic acid,

while less than 5% of epoxide groups participate in said addition reaction.

Liquid emulsion of polyaminoamide curing agent in water or in aqueous copolymer dispersion is preferably prepared with an addition of from 1 to 10 parts by wt. of salicylic acid or lactic acid, said acid being preferably used in a form of a salt with aliphatic or cycloaliphatic amine bearing at least one primary or secondary amine group in the molecule.

The adhesives thus prepared exhibit a bonding ability at temperatures as low as 1-15°C.

In particular cases, 5 to 50 parts of fillers per 100 parts of the dispersion, such as kaolin and bentonite, as well as 2 to 40 parts of commonly known emulsifiers, natural and synthetic resins such as casein, gum acids esters, coumarone resins, urea-formaldehyde resins and melamine-formaldehyde resins per 100 weight parts (pph) of the copolymer may be used in the process of manufacturing the adhesives according to this invention.

EXAMPLES

Example I

Preparation of component I:

1000 g of aqueous dispersion of acrylic copolymer (Acronal V-271) having a glass transition temperature of -25°C is added stepwise to 100 g of the liquid epoxide resin (Epidian 5) while stirring the mixture continuously.

Preparation of component II:

50 g of water is added to 50 g of polyaminoamide (Versamid 140) while stirring the mixture continuously. Then, 100 g of the acrylic copolymer (Acronal V-271) and 190 g of water are added stepwise. Both components are liquid. Before the adhesive is applied, the components I and II are blended using a 3:1 weight ratio (respectively). The adhesive is liquid. When the adhesive is used to bond PVC flooring to fresh, wet concrete substrate, satisfactory bond strength and water resistance of the adhesive bonds is achieved.

Example II

Preparation of component I:

3g of propylamine is added to 100 g of the liquid epoxide resin (Epidian 5) and after 1 hour, 1000 g of Acronal V-271 is added while stirring the mixture continuously.

Preparation of component II:

100 g of water is added slowly to 100 g of the polyaminoamide (Versamid 125) while stirring the mixture continuously followed by the addition of 200 g of Acronal V-271, 100 g of chalk and 100 g of water.

After components I and II are blended using 2:1 weight ratio, a thixotropic adhesive is obtained. When the adhesive is used to bond PVC flooring to green concrete substrate, satisfactory bond strength and water resistance of the adhesive bonds are achieved.

Example III

Preparation of component I:

1000 g of Acronal V-271 is added stepwise to 180 g of the liquid epoxide resin (Epikote 828) while stirring the mixture continuously.

Preparation of component II:

30 g of water and then 90 g of Acronal V-271 and 200 g of water were added to 90 g of Versamid 125. After the components I and II are blended using 10:4 weight ratio, a thixotropic adhesive of good spreadability onto the substrate to be bonded is obtained.

The adhesive has 3 days pot-life and 2 hrs. open time (after applying onto wet concrete substrate) at 20°C. At bonding PVC tiles to wet concrete at 20°C, the initial bonding time amounts to 24 hrs. Complete curing time is 7 days. When such bonded specimen is soaked in water, no damage of the bond is observed during 6 weeks.

Example IV

Preparation of component I:

1000 g of Acronal V-271 is added to 180 g of Epidian 5.

Preparation of component II:

5 g of salicylic acid - isophorone diamine salt is added to 90 g of Versamid 125 followed by the addition of 70 g of water and 90 g of Acronal V-271 and then 100 g of water.

After the components I and II are blended using a 10:3 weight ratio, a thixotropic adhesive is obtained. When the adhesive is applied to wet concrete substrate, the open time is 3 hours at 5°C. Initial curing time is 24 hours.

Full curing time is 7 days. When such bonded specimen is immersed in water, no damage of the bond is observed during 6 weeks.

Example V

Preparation of component I:

1000 g of aqueous dispersion of the acrylic copolymer (Acronal 80-D) having a glass transition temperature of -25°C was added to 180 g of Epidian 5 while stirring the mixture continuously.

Preparation of component II:

50 g of water, 50 g of Acronal 80-D and 40 g of Acronal V-271, and then 200 g of water are added to 90 g of Versamid 125 while stirring the mixture continuously.

After components I and II are blended using a 10:4 weight ratio, a thixotropic adhesive of good spreadability onto both wet concrete substrate and PVC tiles is obtained. Adhesive open time is 1.5 hour at 20°C. Full curing time is 7 days. After that time, the immersion in water for 6 weeks does not result in a damage of the adhesive bond.

Example VI

Preparation of component I:

3 g of lactic acid is introduced to 180 g of Epidian 5 and the mixture is heated up to 80°C, cooled and 1000 g of aqueous dispersion of chloroprene copolymer (Neoprene Latex 115 - du Pont de Nemours & Company) having a glass transition temperature of -14°C is added while stirring the mixture continuously.

Preparation of component II:

90 g of the above aqueous chloroprene copolymer dispersion and 250 g of water are introduced to 90 g of Versamid 125, while stirring the mixture continuously. After components I and II are blended using a 10:4 weight ratio, a thixotropic adhesive is obtained. The adhesive open time (after applying to wet concrete) is 1.5 hour at room temperature. Full curing time is 7 days. After that time, the immersion in water for 6 weeks does not damage the adhesive bond.

Example VII

Preparation of component I:

1000 g of an aqueous dispersion of an ethylene vinyl acetate copolymer (Vinnapas EP-1) having glass transition temperature of -5°C is added to 180 g of Epidian 5 while stirring the mixture continuously.

Preparation of component II:

30 g of the dispersion (Vinnapas EP-1) and then 90 g of the same dispersion (Vinnapas EP-1) and 220 g of water are added to 90 g of Versamid 125.

Both components are liquid. After the component I and II are blended using 10:4 weight ratio and the adhesive is applied to wet concrete substrate, the adhesive open time is 1.5 hour. Initial curing time is 12 hours. After 72 hours, the adhesive bond is resistant to long-term water exposure.

WHAT IS CLAIMED IS:

1. A method of manufacturing a water-resistant, aqueous dispersion-based adhesive, the main component of said adhesive being ethylene vinyl acetate copolymer or an acrylic ester copolymer, or a chloroprene copolymer, optionally containing also fillers, natural and synthetic resins and other additives which comprises introducing 5 to 50 weight parts of epoxide resin or a modified epoxide resin per 100 weight parts of said copolymer to aqueous dispersion of ethylene vinyl acetate copolymer, or of acrylic ester copolymer, or of chloroprene copolymer, said copolymers having a glass transition temperature below -5°C, and separately emulsifying either a liquid polyaminoamide curing agent in water or in an aqueous dispersion of the same copolymer, while using 20 to 100 weight parts of polyaminoamide per 100 weight parts of epoxide resin, optionally of a modified epoxy resin, and blending both components of the adhesive not later than 8 hours before it is applied to the substrates to be bonded.

2. A method of claim 1 wherein epoxide resin is modified by the addition of an aliphatic or a cycloaliphatic amine or aminoalcohol, said amine or aminoalcohol bearing a primary or secondary amino group, or by the addition of a carboxylic acid, 2 to 20 weight parts of said amine, alcoholamine or acid being used per 100 weight parts of epoxide resin.

3. A method of claim 1 or 2 wherein liquid polyaminoamide curing agent is modified by the addition of salicylic acid or lactic acid or their salts with aliphatic or cycloaliphatic amines, 1 to 10 weight parts of said modifying additives being used per 100 weight parts of polyaminoamide.

INTERNATIONAL SEARCH REPORT

International Application No PCT/PL 93/00002

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C09J115/02; C09J123/08; C09J133/06

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C09J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	EP,A,0 338 205 (KAWASAKI STEEL CORPORATION) 25 October 1989 see claims 1-2	1
A	EP,A,0 056 452 (NATIONAL STARK AND CHEMICAL CORPORATION) 28 July 1982 see page 11, line 9 - line 15 see claims 1-4,6-7	1

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
09 JULY 1993	03.08.93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	SIEMENS T.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

PL 9300002
SA 71854

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 09/07/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0338205	25-10-89	AU-B- 611766	20-06-91
		AU-A- 3013589	23-08-90
		US-A- 5008308	16-04-91
EP-A-0056452	28-07-82	US-A- 5037700	06-08-91
		AU-B- 527081	17-02-83
		AU-A- 7943482	29-07-82
		CA-A- 1210182	19-08-86
		JP-C- 1418635	22-12-87
		JP-A- 58029871	22-02-83
		JP-B- 62025196	02-06-87