

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No 03-048026

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**

PCT FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No 533

DE FECHA 31 DE OCTUBRE DE 2003 EL TERMINO HABIL EÑALADO POR LA

LEY EXPIRA EL 30 DE ENERO DEL 2004

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

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Bogotá D.C, SEPTIEMBRE DE 2007

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WELTORGANISATION FÜR GEISTIGES EIGENTUM
Internationales Büro
INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

(51) Internationale Patentklassifikation ⁶ : C09D 7/12, 201/06, B05D 7/16		A1	(11) Internationale Veröffentlichungsnummer: WO 98/58029
			(43) Internationales Veröffentlichungsdatum: 23. Dezember 1998 (23.12.98)
(21) Internationales Aktenzeichen: PCT/EP98/03463 (22) Internationales Anmeldedatum: 9. Juni 1998 (09.06.98) (30) Prioritätsdaten: 197 25 742.9 18. Juni 1997 (18.06.97) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): HERBERTS GESELLSCHAFT MIT BESCHRÄNKTER HAF- TUNG [DE/DE]; Christbusch 25, D-42285 Wuppertal (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): BRENKE, Stephan [DE/DE]; Am Eckbusch 49, D-42113 Wuppertal (DE). DÖSSEL, Karl-Friedrich [DE/DE]; Hardtstrasse 135, D-42107 Wuppertal (DE). HERRMANN, Friedrich [DE/DE]; Friedrichsallee 27, D-42117 Wuppertal (DE). REIFFERSCHIEDT, Heinz-Walter [DE/DE]; Immanuel-Kant-Strasse 39, D-44803 Bochum (DE). (74) Anwalt: TÜRK GILLE HRABAL LEIFERT; Brucknerstrasse 20, D-40593 Düsseldorf (DE).		(81) Bestimmungsstaaten: AU, BR, CA, CZ, JP, KR, MX, PL, SI, US, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i>	
(54) Title: TRANSPARENT COATING AGENTS AND THE USE THEREOF TO PRODUCE MULTI-LAYERED COATINGS (54) Bezeichnung: KLARLACKÜBERZUGSMITTEL UND DEREN VERWENDUNG ZUR HERSTELLUNG VON MEHRSCHICHT-LACKIERUNGEN (57) Abstract The invention relates to transparent coating agents suitable for multi-layered coatings, containing self-crosslinking or external crosslinking bonding agents, organic solvents, various crosslinking agents in the case of external crosslinking bonding agents formaldehyde condensation resins, in addition to optional reactive diluents and usual varnish additives with an additional content of A) 0.1 to 3 wt. % urea compounds and B) 0.05 to 10 wt. % substances providing formaldehyde, in relation to solid resin bodies formed by the bonding agents, reactive diluents and crosslinking agents. (57) Zusammenfassung Für Mehrschichtlackierungen geeignete Klarlacküberzugsmittel, enthaltend selbstvernetzende oder fremdvernetzende Bindemittel, organische Lösemittel, im Falle von fremdvernetzenden Bindemitteln von Aldehyd-Kondensationsharzen unterschiedliche Vernetzer, sowie gegebenenfalls Reaktivverdünner und für Klarlacke übliche Additive mit einem zusätzlichen Gehalt von A) 0,1 bis 3 Gew.-% Harnstoffverbindungen und B) 0,05 bis 10 Gew.-% Formaldehyd liefernde Substanzen, jeweils bezogen auf den durch Bindemittel, Reaktivverdünner und Vernetzer gebildeten Harzfestkörper.			

Ethylenglykoldimethylether; Glykoletherester, wie Ethylglykolacetat, Butylglykolacetat, 3-Methoxy-n-butylacetat, Butyldiglykolacetat, Methoxypropylacetat; Ester, wie Butylacetat, Isobutylacetat, Amylacetat; Ketone, wie Methylethylketon, Methylisobutylketon, Diisobutylketon, Cyclohexanon, Isophoron; Alkohole, wie Methanol, Ethanol, Propanol, Butanol; aromatische Kohlenwasserstoffe, wie Xylol, Solvesso 100 (eingetragenes Warenzeichen für ein Gemisch aromatischer Kohlenwasserstoffe mit einem Siedebereich von 155 bis 185°C) und aliphatische Kohlenwasserstoffe.

Die erfindungsgemäßen Klarlacküberzugsmittel enthalten bezogen auf ihren Harzfestkörper 0,1 bis 3, bevorzugt 0,3 bis 2, besonders bevorzugt 0,5 bis 1,5 Gew.-% einer oder mehrerer Harnstoffverbindungen (A) als Antiablaufmittel, d.h. als thixotropierend wirkende oder Strukturviskosität bewirkende Mittel, welche das Ablaufverhalten der Klarlacküberzugsmittel günstig beeinflussen. Sie verhindern das unerwünschte Abfließen oder Absacken von aus den erfindungsgemäßen Klarlacküberzugsmitteln auf senkrechten Flächen aufgetragenen Klarlackschichten wirksam.

Bei den Harnstoffverbindungen (A) handelt es sich um als Antiablaufmittel beispielsweise aus den DE-C-27 51 761, EP-A-0 192 304 und EP-A-0 198 519 bekannte Harnstoffverbindungen, die in Einbrennklarlacken eingesetzt werden können. Bei Einbrennklarlacken tritt das Ablaufproblem insbesondere während des Einbrennprozesses durch eine anfängliche temperaturbedingte Viskositätserniedrigung in Erscheinung.

Bei den Harnstoffverbindungen (A) handelt es sich um Additionsprodukte aus aromatischen, araliphatischen, cycloaliphatischen oder aliphatischen Diisocyanaten und/oder davon abgeleiteten Polyisocyanaten (beispielsweise solche vom Isocyanurat-Typ) und Mono- und/oder Polyaminen mit primären und/oder sekundären Aminogruppen. Bei den Additionsprodukten kann es sich um definierte niedermolekulare Verbindungen oder oligomere oder polymere Additionsprodukte handeln. Bevorzugte Harnstoffverbindungen (A) sind solche, bei denen Polyisocyanat

brilliant und trübungsfrei.

Herstellung von Mehrschichtlackierungen

Vergleichsbeispiel A

~~Zunächst wird in üblicher Weise durch Vermischen einer Acrylatharzlösung mit Additiven und Lösemitteln ein Stammlack mit folgender Zusammensetzung hergestellt:~~

~~42 Teile Acrylatfestharz (Hydroxylzahl 140 mg KOH/g)~~

~~1 Teil Lichtschutzmittel (Benzotriazolderivat)~~

~~1 Teil Lichtschutzmittel (HALS-Derivat, HALS = hindered amine light stabiliser)~~

~~0,2 Teile handelsübliches Silikonöl als Verlaufsmittel (berechnet als Wirksubstanz)~~

~~55,8 Teile eines Gemischs organischer Lösemittel.~~

Durch Vermischen von 100 Teilen des Stammlacks mit 30 Teilen einer Härterlösung, bestehend aus 24,6 Teilen Triisocyanat (Hexamethylendiisocyanat-Isocyanurat) und 5,4 Teilen Butylacetat wird ein Klarlack hergestellt.

Auf ein mit einer Kataphoresegrundierung und Füllerschicht versehenes Blech wird ein schwarzer Uniwasserbasislack in einer Trockenschichtdicke von 16 μm aufgespritzt und 10 Minuten bei 80°C vorgetrocknet. Dann wird der vorstehend beschriebene Klarlack keilförmig auf das hängende Blech aufgespritzt mit einem Schichtdickengradienten von 10 bis 70 μm Trockenschichtdicke. Nach 10 Minuten Ablüften bei Raumtemperatur wird 20 Minuten bei 140°C (Objekttemperatur) eingebrannt. Das Blech befindet sich bei allen Operationen in der senkrechten Position.

Vergleichsbeispiel B

Zunächst wird ein Stammlack mit gleichem Gewichtsfestkörper wie in



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85**United States Patent** [19]**Ohashi et al.**[11] **Patent Number:** **5,698,656**[45] **Date of Patent:** **Dec. 16, 1997****[54] MOISTURE-CURING URETHANE ADHESIVE COMPOSITION**[75] **Inventors:** Yoshinobu Ohashi; Hideyuki Matsuda; Eiji Nishi; Tsuyoshi Nishida, all of Hiratsuka, Japan[73] **Assignee:** The Yokohama Rubber Co., Ltd., Tokyo, Japan[21] **Appl. No.:** 554,711[22] **Filed:** Nov. 7, 1995**[30] Foreign Application Priority Data**Dec. 7, 1994 [JP] Japan 6-303779
Dec. 20, 1994 [JP] Japan 6-317127[51] **Int. Cl.⁶** C09J 175/06; C09J 175/08; C08G 18/12; C08G 18/30[52] **U.S. Cl.** 528/49; 525/457; 525/458; 528/45; 528/59; 528/67; 528/77; 528/80; 528/905[58] **Field of Search** 525/457, 458; 528/45, 49, 59, 67, 77, 80, 905**[56] References Cited****U.S. PATENT DOCUMENTS**4,083,815 4/1978 Thompson 524/290
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2-182774 7/1990 Japan .
3-59084 3/1991 Japan .
5-171035 7/1993 Japan .
6-88067 3/1994 Japan .*Primary Examiner*—Rabon Sargent*Attorney, Agent, or Firm*—Finnegan, Henderson, Farabow, Garrett & Dunner

[57]

ABSTRACT

A moisture-curing urethane adhesive composition of a urethane prepolymer resulting from the reaction of a mixture of a polyether diol and a polyether triol with a diisocyanate compound, and a polyurethane compound resulting from the reaction of a mixture of a polyester polyol and a polypropyleneether polyol with a hexamethylene diisocyanate compound with addition of a monoalcohol. A modified moisture-curing urethane adhesive composition of a urethane prepolymer resulting from the reaction of a mixture of a polyether diol and a polyether triol with a diisocyanate compound, a first polyurethane compound resulting from the reaction of a copolymeric polyol consisting of propylene oxide and ϵ -caprolactone with a hexamethylene diisocyanate compound with addition of a monoalcohol, and a second polyurethane compound resulting from the reaction of a polyester polyol with a hexamethylene diisocyanate compound with addition of a monoalcohol.

2 Claims, No Drawings

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MOISTURE-CURING URETHANE ADHESIVE COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to moisture-curing hot-melt urethane adhesive compositions and has particular reference to such an adhesive or sealant composition useful for bonding inter alia windshields in place on an automotive vehicle.

2. Prior Art

There are known various reactive hot-melt polymer compositions which are applied in the molten state to induce initial structural strength upon solidification with temperature drop and subsequently exhibit final bond strength and elasticity upon curing. These peculiar physical properties contribute to a wide range of application of such hot-melt compositions as adhesives or sealants in various sectors of the industry such as automobile, textile, wood, construction and so on. Reactive hot-melts have found most extensive use as sealants for direct glazing automobile windshields, in which instance the sealant is required to be free of sagging; i.e. initially dimensionally stable when applied and exhibit high final bond strength when cured.

As disclosed for instance in Japanese Laid-Open Patent Publication No. 2-32189, a moisture-curing hot-melt sealant is made up predominantly of a polyether polyol-based urethane prepolymer in which a polyether polyol is used in combination with a polyester polyol.

Japanese Laid-Open Patent Publication No. 3-59084 discloses a moisture-curing hot-melt adhesive comprising a block urethane prepolymer derived from reacting a diisocyanate compound with a mixture of a polyol of less than 8,000 molecular weight and a block polymer polyol resulting from the reaction of a terminal isocyanate group-containing urethane prepolymer with a thermoplastic saturated polyester polyol, the urethane prepolymer being blended with another terminal isocyanate group-containing urethane prepolymer.

Japanese Laid-Open Patent Publication No. 2-182774 discloses a fast-curing hot-melt polyurethane composition derived from blending a polyether polyol having a relatively small molecular weight and a higher glass transition point than room temperature with a urethane prepolymer having a relatively large molecular weight and a lower glass transition point than room temperature.

Japanese Laid-Open Patent Publication No. 6-88067 discloses that a sealant composition comprising a blend of a polyether polyol-based urethane prepolymer and an ester compound melting at 30°-100° C. can exhibit high initial structural strength with least moist heat deterioration.

Japanese Laid-Open Patent Publication No. 5-171035 discloses a moisture-curing urethane sealant composition comprising a urethane prepolymer blended with a urethane compound containing a polyether polyol or a polyester polyol and isocyanates with addition of a monoalcohol to hinder free isocyanate groups in the prepolymer, the resulting product being described as possessing fast setting, high initial adhesion strength and after-cure bond and elastic properties.

The prior art adhesive or sealant compositions referred to above are not entirely satisfactory because those comprising urethane prepolymers tend to become too viscous as their application temperature is rather high, while those containing hindered isocyanate materials would fail to retain final bond strength and rubber-like elasticity as desired in the cured product.

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SUMMARY OF THE INVENTION

Whereas, the present invention seeks to provide a moisture-curing urethane adhesive composition which will exhibit sufficient initial structural strength in the uncured state to achieve a maximum rate of working efficiency and a high final bond strength in the cured state, or such hot-melt properties that meet the necessary requirements for inter alia direct glazing of automobile windshields.

According to a first embodiment of the invention, there is provided a moisture-curing urethane adhesive composition comprising (A) a urethane prepolymer resulting from the reaction of a mixture of a polyether diol and a polyether triol both having a number-average molecular weight of from 1,000 to 7,000 with a diisocyanate compound in an equivalent ratio of isocyanate group/hydroxyl group of between 1.1 and 2.5; and (B) a polyurethane compound resulting from the reaction of a mixture of a polyester polyol having a number-average molecular weight of from 500 to 6,000 and a polypropyleneether polyol having a number-average molecular weight of from 1,000 to 7,000 with a hexamethylene diisocyanate compound in an equivalent ratio of isocyanate group/hydroxyl group of between 1.5 and 2.5 to form an isocyanate prepolymer with addition of a monoalcohol having a carbon number of from 1 to 22 the equivalent ratio of hydroxyl groups in the monoalcohol to isocyanate groups in the isocyanate prepolymer being less than 0.9; the polyurethane compound (B) being present in an amount of from 1 to 20 parts by weight per 100 parts by weight of the urethane prepolymer (A).

According to a second embodiment of the invention, there is provided a moisture-curing urethane adhesive composition comprising (A) a urethane prepolymer resulting from the reaction of a mixture of a polyether diol and a polyether triol both having a number-average molecular weight of from 1,000 to 7,000 with a diisocyanate compound in an equivalent ratio of isocyanate group/hydroxyl group of between 1.1 and 2.5; (B') a polyurethane compound resulting from the reaction of a copolymeric polyol consisting of a blend of propylene oxide and ϵ -caprolactone, said copolymeric polyol having a number-average molecular weight of from 1,000 to 3,000 and being blended in a mole ratio of from 8/2 to 2/8, with a hexamethylene diisocyanate compound in an equivalent ratio of isocyanate group/hydroxyl group of between 1.5 and 2.5 to form an isocyanate prepolymer with addition of a monoalcohol having a carbon number of from 1 to 22 the equivalent ratio of hydroxyl groups in the monoalcohol to isocyanate groups in the isocyanate prepolymer being less than 0.9; and (C) a polyurethane compound resulting from the reaction of a polyester polyol having a number-average molecular weight of from 1,000 to 7,000 with a hexamethylene diisocyanate compound in an equivalent ratio of isocyanate group/hydroxyl group of between 1.5 and 2.5 to form an isocyanate prepolymer with addition of a monoalcohol having a carbon number of from 1 to 22 the equivalent ratio of hydroxyl groups in the monoalcohol to isocyanate groups in the isocyanate prepolymer being less than 0.9; the weight ratio of compound (B') to compound (C) being in the range of from 0.1:1 to 5:1, and the sum of compound (B') and compound (C) being in the range of from 1 to 20 parts by weight per 100 parts by weight of prepolymer (A).

DETAILED DESCRIPTION OF THE INVENTION

The moisture-curing urethane-based adhesive or sealant composition according to the first embodiment of the present

invention is made up essentially of a selected urethane prepolymer (A) and a selected polyurethane compound (B) blended together in certain specified amounts.

Urethane Prepolymer (A)

This prepolymer is derivable from reacting a mixture of polyether diol and triol each having a number-average molecular weight of from 1,000 to 7,000 with a diisocyanate in an equivalent ratio of isocyanate group/hydroxyl group of between 1.1 and 2.5. The polyol mixture is obtainable from addition reaction of one or more alkylene oxides such as ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran and the like with two or more active hydrogen atom-containing compound such as polyalcohols, amines, alkanolamines and polyphenols, said polyalcohols including ethylene glycol, propylene glycol, butane diol, diethylene glycol, glycerin, hexane triol, trimethylol propane, pentaerythritol and the like, said amines including ethylene diamine, hexamethylene diamine and the like, said alkanolamines including ethanolamine, propanolamine and the like, and said polyphenols including resorcinol, bisphenol and the like. The use of such diol and triols in appropriate balanced amounts is conducive to suppressing objectionable foaming thanks to their ability to form a three-dimensional cross-linkage.

It has been found that the number-average molecular weight of each of polyether triol and polyether diol useful in the preparation of the urethane prepolymer (A) should be in the range of 1,000-7,000, failing this would result in a prepolymer being too viscous with number-average molecular weights smaller than 1,000 and in a resultant composition being degraded in after-cure bond strength with molecular weights larger than 7,000. The mole ratio of polyether triol to polyether diol is preferably in the range of from 1:3 to 3:1 to provide satisfactory viscosity, curing and final product properties.

The diisocyanate compound used as a co-reactant in the preparation of the urethane prepolymer (A) may be chosen from those commonly accepted for the manufacture of urethane resins. Specific examples include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, phenylene diisocyanate, xylene diisocyanate, diphenylmethane-4,4'-diisocyanate, naphthalene-1,5-diisocyanate and hydrogones thereof, ethylene diisocyanate, propylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, 1-methyl-2,4-diisocyanate cyclohexane, 1-methyl-2,6-diisocyanate cyclohexane, dicyclohexylmethane diisocyanate, triphenylmethane triisocyanate and the like. These compounds may be used alone or in combination.

The polyether polyol is reacted with the diisocyanate compound in an equivalent ratio of isocyanate group to hydroxyl group of 1.1 to 2.5. Smaller ratios would render prepolymer (A) too viscous to warrant practical application. Greater ratios would leave much polyisocyanate compound unreacted, causing insufficient resistance to foaming during sealant formulation. Though not specifically restricted, the reaction may be effected in conventional manner, for example, at a temperature of about 50° to 100° C. and under atmospheric pressure and if necessary with use of a urethane catalyst such as a tin or bismuth compound of an organic class.

Polyurethane Compound (B)

This compound is derivable from reacting a mixture of polyether polyol having a number-average molecular weight of from 500 to 6,000 and a polypropyleneether polyol having a number-average molecular weight of from 1,000 to 7,000 with a hexamethylene diisocyanate compound in an

equivalent ratio of isocyanate group/hydroxyl group of between 1.5 and 2.5 to produce a urethane or isocyanate prepolymer followed by the addition of a monoalcohol having a carbon number of from 1 to 22 in an equivalent ratio of hydroxyl group/isocyanate group of less than 0.9.

The polyester polyol useful in the preparation of the urethane prepolymer may be a polycondensate of a polybasic acid such as a dibasic acid with a polyhydroxyl compound such as a glycol. Suitable polybasic acids include adipic acid, sebacic acid, phthalic acid, maleic acid, glutaric acid and the like. Polyhydroxyl compounds typically include ethylene glycol, diethylene glycol, butylene glycol, neopentyl glycol, hexane glycol, trimethylol propane, glycerine pentaerythritol and the like. Polyester polyols other than the polycondensate may be suitably used such as a polycarbonate polyol having two alkylene groups bonded side by side via a carbonate linkage and a lactone-type polyester polyol obtained by ring open polymerization of a monomeric caprolactone. The polyester polyol has a number-average molecular weight of 500 to 6,000. Smaller than 500 molecular weights would lead to increased crystallinity and higher melting point of the resultant product. Larger than 6,000 molecular weights would result in reduced adhesion to a substrate.

The propyleneether polyol referred to hereunder includes a polyol such as diols and triols that may be derived from the addition reaction of propylene oxide with a compound having two or more active hydrogen atoms, this compound being the same as used in the preparation of the polyether polyol in the urethane prepolymer (A). Number-average molecular weights of these polyols if smaller than 1,000 would lead to objectionably high viscosity of the resultant prepolymer and if larger than 7,000 would retard crystallization of the reaction product and lose the initial structural strength. The polypropyleneether polyol is chosen in the invention so as to maintain compatibility with the urethane prepolymer (A).

The mole ratio of polyester polyol to polypropyleneether polyol is in the range of 1:1 to 10:1, preferably 2:1 to 5:1. Ratios less than 1 would fail to achieve appropriate initial structural strength and greater than 10 would result in reduced dispersability of the polyester in the urethane compound (B), leading to reduced bonding strength.

The choice of hexamethylene diisocyanate (HDI) for use in the preparation of the urethane or isocyanate prepolymer is attributed to its contribution to improved initial structural strength of the inventive hot-melt adhesive composition.

The equivalent ratio of isocyanate groups in the hexamethylene diisocyanate compound to hydroxyl groups in the polyols is selected to be in the range of from 1.5 to 2.5. Ratios smaller than 1.5 would lead to excessive viscosity and hence less compatibility with the co-reactant urethane prepolymer (A), while ratios greater than 2.5 would result in retarded crystallization and loss of the initial structural strength, a cause for sagged coat.

The polyurethane compound (B) results from the reaction of the urethane or isocyanate prepolymer with such a monoalcohol which is capable of hindering at least part of the isocyanate groups in the diisocyanate compound.

Monoalcohols eligible for the purpose of the invention include straight or branched chain, saturated or unsaturated monoalcohols. Preferred examples are straight-chain saturated alcohols of 2-12 carbon atoms such as methanol, ethanol, butanol, isobutanol, propanol, pentanol, hexanol, heptanol, octanol, stearyl alcohol, benzyl alcohol, 2-hydroxymethyl-methacrylate and the like. The equivalent ratio of hydroxyl groups in the monoalcohol to isocyanate

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groups in the urethane or isocyanate prepolymer is less than 0.9, preferably in the range of from 0.1 to 0.5. Ratios greater than 0.9 would result in reduced bond strength.

The reaction for hindering or eliminating free isocyanates in the formulation of the polyurethane compound (B) may be similar to that of urethanation effected at a temperature of 50°–100° C. under atmospheric pressure.

The polyurethane compound (B) is used in an amount of 1–20 parts by weight per 100 parts by weight of the urethane prepolymer (A). Amounts smaller than 1 weight part would fail to develop the requisite initial structural strength, while amounts larger than 20 weight parts would result in reduced bond strength and degraded rubber-like property of the adhesive composition in the cured state.

In the practice of the invention, there may be used various additives commonly known in the art which include plasticizers, fillers, thixotropic agents, tackifiers, catalysts, ultraviolet absorbers, dyes, pigments, flame retardants and the like. Typical plasticizers are chosen from derivatives of benzoic acid, phthalic acid, trimellitic acid, pyromellitic acid, adipic acid, sebacic acid, fumaric acid, maleic acid, itaconic acid and citric acid and of polyester, polyether and epoxy and the like. Suitable fillers are silicic acid derivatives, talc, metallic powder, calcium carbonate, clay, carbon black and the like. Thixotropic agents typically include benton, anhydrous silicic acid, urea derivatives and the like. Eligible catalysts include dibutyltin dilaurate, dioctyltin dilaurate, zinc octylate, organic bismuth compounds, triethyldiamine, amine compounds such as morpholine amine and the like.

A preferred formulation of the inventive hot-melt sealant according to the first embodiment of the invention exemplarily comprises 1–20 parts by weight of the polyurethane compound (B) per 100 parts by weight of the urethane prepolymer (A), less than 20 percent by weight of a plasticizer, less than 60 percent by weight of a filler and less than 3 percent by weight of other additives, the amounts of the urethane prepolymer (A) and the polyurethane compound (B) being 20–70 percent by weight and less than 14 percent by weight, respectively, based on total composition.

The adhesive or sealant composition according to the invention may be prepared exemplarily by the process in which the urethane prepolymer (A) and the polyurethane compound (B) are introduced into a kneader loaded with nitrogen gas, followed by the addition of plasticizers, fillers and other additives as deemed necessary or desirable, the whole being kneaded sufficiently in vacuum and kneading is continued with the addition of a catalyst if necessary.

The resulting composition in the molten state may be applied per se to a substrate, or alternatively taken into a suitable container, cooled and sealed for storage. The thus stored composition can be melted with heat to be readily applied to a desired substrate. When installing a windshield in a car, the sealant composition is coatable at about 50°–60° C. over either or both of the glass pane and the window frame and allowed to cool and harden, retaining sufficient structural strength to avoid sagging and finally cured upon exposure to environmental moisture, exhibiting the required bond strength and elasticity.

The invention will be further described by way of the following examples.

INVENTIVE EXAMPLES 1–11 and COMPARATIVE EXAMPLES 1–6

The formulations and property test results of several inventive sealants and some controls are shown in Table 1 and Table 2, respectively.

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For purposes of illustration, the viscosity of the composition in Inventive Example 2 was 1,410 poise (Ps) at 20° C. and 230 Ps at 60° C.; that in Inventive Example 4 was 1,630 Ps at 20° C. and 250 Ps at 60° C.; that in Inventive Example 6 was 1,320 Ps at 20° C. and 220 Ps at 60° C.; and that in Comparative Example 4 was 600 Ps at 20° C. and 210 Ps at 60° C.

Preparation of Urethane Prepolymer (A)

57 parts by weight of a polyoxypropylene triol having three hydroxyl groups and an average molecular weight of 5,000 and 23 parts by weight of a polypropylene ether diol having two hydroxyl groups and an average molecular weight of 2,000 were charged into a reactor and subjected to dehydration at 110° C. and under 50 mmHg for two hours. The admixture was then cooled, followed by the addition of 9.1 parts by weight of a mixture of 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate (80:20) with stirring. The reaction was continued until free isocyanates were held to 2.2%, thereby providing a toluene diisocyanate (TDI) prepolymer. This prepolymer was stirred together with 19.6 parts by weight of diphenylmethane-4,4'-diisocyanate, followed by the addition of 85 parts by weight of prehydrated polyoxypropylene triol having an average molecular weight of 5,000 and 35 parts by weight of a polypropylene ether diol having an average molecular weight of 2,000. The reaction was continued at 80° C. until free isocyanates were diminished to 1.8%, thereby providing a 4,4'-diphenylmethane diisocyanate (MDI) prepolymer.

Preparation of Polyurethane Compound (B)

Polycaprolactone polyol having an average molecular weight of 3,000 and polypropylene ether polyol having an average molecular weight of 2,000 were taken in the tabulated mole ratio and quantity into a reactor and subjected to dehydration at 110° C. and under 50 mmHg for two hours. The admixture was cooled to 80° C., followed by the addition with stirring of hexadimethylene diisocyanate of the tabulated mole ratio. The mixture was further added with ethanol of the tabulated mole ratio, and the reaction was continued until all free isocyanates were substantially hindered.

Preparation of Moisture-Curing Sealant Composition

A nitrogen-filled kneader was charged with 100 parts by weight of each urethane prepolymer (A) and tabulated parts by weight of each polyurethane compound (B), followed by addition of 20 weight parts dehydrated plasticizer (triethyl trimellitate), 100 weight parts dry carbonblack and 10 weight parts dry calcium carbonate. Sufficient kneading was continued in vacuum with the addition of 1.7 weight parts 50% dioctylphthalate solution of dioctyl-tin-laurate.

Initial Structural Strength Test

The various tabulated sealant compositions were tested for tensile strength by disposing each test sample at a temperature of 20° C. and a relative humidity of 65% and for a period of 10 minutes, the test sample having been warmed to 60° C. and coated over a glass substrate and squeezed between a pair of glass plates to a bond thickness of 6 mm.

Final Bond Strength Test

Each of the tabulated compositions was applied over a primer-coated sheet of glass and over a primer-coated sheet of steel, respectively, to a coat thickness of 3 mm and disposed at a temperature of 20° C. and a relative humidity of 65% for a period of 7 consecutive days. Test samples were each tested for material breakage and surface peel by observing tensile break behavior along knife-cut lines.

The moisture-curing urethane adhesive or sealant composition according to the second embodiment of the invention is made up essentially of a urethane prepolymer (A) and two different polyurethane compounds (B') and (C).



US005473043A

United States Patent [19]

Maki et al.

[11] Patent Number: **5,473,043**[45] Date of Patent: **Dec. 5, 1995**[54] **MOISTURE-CURABLE URETHANE RESIN COMPOSITIONS**[75] Inventors: **Hirohisa Maki, Otsu; Shigenobu Miyamoto, Kameoka; Ryoji Fujimoto; Toshiki Noda**, both of Kyoto, all of Japan[73] Assignee: **Dai-Ichi Kogyo Seiyaku Co., Ltd.**, Kyoto, Japan[21] Appl. No.: **226,003**[22] Filed: **Apr. 8, 1994**[30] **Foreign Application Priority Data**Apr. 9, 1993 [JP] Japan 5-083028
Apr. 28, 1993 [JP] Japan 5-124994[51] Int. Cl.⁶ **C08G 18/10**[52] U.S. Cl. **528/60; 528/65; 528/66; 524/59; 524/589; 524/592; 524/593; 524/597**[58] Field of Search **528/60, 65, 66; 524/59, 589, 592, 593, 597**[56] **References Cited****U.S. PATENT DOCUMENTS**

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5-8730 2/1993 Japan .*Primary Examiner*—James J. Seidleck*Assistant Examiner*—Duc Truong*Attorney, Agent, or Firm*—Marshall, O'Toole, Gerstein, Murray & Borun[57] **ABSTRACT**

Moisture-curable urethane resin compositions comprising: (a) a urethane prepolymer having two or more terminal isocyanate groups, (b) a blocked amine compound which is essentially nonreactive with an isocyanate group and generates a primary or a secondary amino group upon contact with water, and (c) an inorganic filler treated with an organic compound, are disclosed. More particularly, the urethane resin compositions comprise a hydrophilic urethane prepolymer having oxyethylene moieties, and a blocked amine compound having two or more oxazolidine rings.

8 Claims, No Drawings

5,473,043

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MOISTURE-CURABLE URETHANE RESIN COMPOSITIONS

FIELD OF THE INVENTION

The present invention relates to moisture-curable urethane resin compositions of the single package-type which are useful as waterproofing agents for roofs, walls, and the like, and as sealants, wall covering materials, paving materials, floor covering materials, coatings and in similar applications.

BACKGROUND OF THE INVENTION

An example of a prior art single package urethane resin composition is a moisture-curable coating-type waterproofing agent, wherein a urethane prepolymer having a terminal isocyanate (NCO) group is mixed with an inorganic filler, as disclosed in Japanese Provisional Patent Publication No. SHO-57-94056, referred to hereinafter as "Prior Art I." In the case of Prior Art I, the NCO group can react with moisture in the air or in the substrate to generate carbon dioxide. The generation of carbon dioxide can cause "blisters", especially when the film coating is thick.

Japanese Patent Publication No. SHO-48-20639 (referred to hereinafter as "Prior Art II") and Japanese Provisional Patent Publication No. HEI-2-55715 (referred to hereinafter as "Prior Art III") disclose oxazolidine-isocyanate compositions. The compositions disclosed in Prior Art II and Prior Art III do not generate carbon dioxide during curing. However, when an oxazolidine-isocyanate composition is mixed with an inorganic filler and stored for a long period, the inorganic filler separates from the composition and settles to form a hard cake. Then, although the composition is a single package coating-type composition, it is necessary to thoroughly stir the composition before application to redisperse the inorganic filler and make the composition homogeneous. A single package coating-type composition provides an advantage only when the composition can be applied without the need to stir the composition before application. If the composition requires stirring before application, there is no advantage to using a single package-type material, and any two package-type composition can be used.

Japanese Patent Publication No. SHO-59-5156 (referred to hereinafter as "Prior Art IV") discloses a composition containing an enamine, and Japanese Patent Publication No. HEI-5-8730 (referred to hereinafter as "Prior Art V") discloses a composition containing a ketimine, respectively. Both Prior Art IV and Prior Art V, however, incorporate standard inorganic fillers which, when stored over a long period, pose disadvantages such as settling of the inorganic filler and slow curing speed.

It also is known that an organic or an inorganic anti-settling agent can be used in conjunction with an inorganic filler to prevent the filler from settling. However, when a commonly-used anti-settling agent is mixed with an oxazolidine-isocyanate composition, the anti-settling agent can retard curing or adversely affect the storage stability of the composition.

The present invention is directed to overcoming the drawbacks and disadvantages of the prior art compositions. An important aspect of the present invention therefore is to provide moisture-curable urethane resin compositions that do not separate and settle in storage, that cure relatively quickly in air, and that do not produce blisters in the film.

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SUMMARY OF THE INVENTION

The moisture-curable polyurethane resin compositions of the present invention are characterized in that the compositions comprise (a) a urethane prepolymer having two or more terminal isocyanate groups, (b) a blocked amine compound which is essentially nonreactive with isocyanate groups and which produces a primary or a secondary amino group upon contact with moisture, and (c) an inorganic filler treated with an organic compound.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with an important feature of the present invention, a urethane prepolymer having at least two terminal isocyanate groups can be, for example, a reaction product of a monohydroxy compound, such as an ethylene oxide adduct of methanol or ethanol, and a polyisocyanate; a reaction product of a compound having two or more active hydrogens and a polyisocyanate; or a single polyisocyanate.

A compound having two or more active hydrogens can be, for example, a polyester polyol having terminal hydroxyl groups produced by condensing a polyol, such as ethylene glycol, propylene glycol, diethylene glycol or trimethylol propane, and a polybasic acid, such as malonic acid, succinic acid, adipic acid or phthalic acid; a low molecular weight polyol, such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol or trimethylol propane; or a compound having hydroxyl groups, like for example, polybutadiene glycol, polyisoprene glycol, lactone ring-opening polymerization products, tetrahydrofuran ring-opening polymerization products, castor oil or a polyol, wherein the mean molecular weight per active hydrogen is preferably from 30 to 100,000. The compound having two or more active hydrogens can be a single compound having two or more active hydrogens or a mixture of compounds having two or more active hydrogens.

The urethane prepolymer having two or more terminal isocyanate groups can be a hydrophilic urethane prepolymer having oxyethylene moieties present in the molecule. A useful hydrophilic urethane prepolymer having at least two free isocyanate groups is obtained by reacting: (1) a polyoxyalkylene alcohol or polyol having an oxyethylene-containing oxyalkylene chain, wherein the oxyethylene moiety content in the oxyalkylene chain is 5 weight percent or greater, with (2) an organic polyisocyanate.

The above-mentioned monohydroxy compound, i.e., alcohol, or polyol can be selected, for example, from an alcohol, such as methanol, ethanol, propanol, butanol, octanol and lauryl alcohol; a diol such as ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol and 1,6-hexanediol; a polyol such as glycerol, trimethylol propane and pentaerythritol; mono-, di- or triethanolamine, diglycerol, sorbitol and sucrose, either singly or in mixture. The polyoxyalkylene alcohol or polyol can be an alcohol or polyol obtained by addition polymerization of ethylene oxide only, or of ethylene oxide with propylene oxide or butylene oxide, according to well known methods, wherein the amount of oxyethylene moieties in the oxyalkylene chain is 5 weight percent or greater, and preferably from 10 to 100 weight percent.

The organic polyisocyanate reacted with the alcohol, the polyol or the compound having two or more active hydrogens, or used as the urethane prepolymer having two or more terminal isocyanate groups, preferably can be polymethylenepolyphenylpolyisocyanate, diphenylmethane diisocyan-

ate, toluene diisocyanate, hexamethylene diisocyanate, xylylene diisocyanate, tetramethylxylylene diisocyanate, isophorone diisocyanate, naphthalene diisocyanate, hydrogenated diphenylmethane diisocyanate, either singly or in mixture, the biuret form, isocyanate form or carbodiimide-modified form. Such organic isocyanates can be used in the form of a crude product.

The hydrophilic urethane prepolymer can be obtained by reacting the alcohol or polyol with the organic polyisocyanate by a method known to those skilled in the art, at an NCO/OH equivalent ratio of 1.5/1 to 100/1, and preferably 2/1 to 50/1. The urethane prepolymer thus obtained typically all has essentially all unreacted isocyanate groups at the terminal ends.

The blocked amine compound that is essentially, and preferably completely, nonreactive with an isocyanate group and produces the primary or the secondary amino group by reacting with water (hereinafter referred to as "blocked amine compound") can be an aldimine, ketimine, enamine, oxazolidine, or similar compound. For example, the blocked amine compound can be a condensate of a compound having at least one primary or secondary amino group and an active oxygen, such as a primary or secondary amino group and a hydroxyl group (hereinafter referred to as the "activated hydrogen compound") and an aldehyde or a ketone, or a compound having two oxazolidine rings obtained from the condensation reaction between an N-hydroxy-oxazolidine and an organic polyisocyanate.

Typical activated hydrogen compounds include, for example, compounds having a primary amino group and a hydroxyl group, compounds having a secondary amino group and a hydroxyl group, compounds having a primary amino group and a secondary amino group, compounds having a primary amino group, a secondary amino group and a hydroxyl group, compounds having two primary amino groups, compounds having two secondary amino groups, and compounds having two secondary amino groups and two hydroxyl groups.

Specific examples of activated hydrogen compounds include, but are not limited to, 2-(2-aminoethoxy) ethanol, N-(2-aminoethyl)piperazine, omega-hydroxyhexylamine, N-methyl-1,6-hexandiamine, diethylenetriamine, N-(2-hydroxyethyl)ethylenediamine, 3-aminoethylpiperidine, N-(2-hydroxyethyl)piperazine, a polyamide obtained from various oils and fats (such as the dimer acid of tall oil fatty acid, and the like) and piperazine anhydride, 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexanone, N-(methylaminoethyl)piperazine, aniline, toluidine, xylidine, isophoronediamine, diaminobenzene, diaminomethylnorbornane, diaminomethylbicycloheptanone, ethanalamine, diethanalamine, dipropanolamine, and hexanolamine.

Aldehydes or ketones to be condensed with activated hydrogen compounds include, for example, acetaldehyde, propionaldehyde, butyraldehyde, trimethylaldehyde, triethylacetaldehyde, valeraldehyde, acrolein, crotonaldehyde, furfural, benzaldehyde, acetone, methyl ethyl ketone, methyl isobutyl ketone, diethyl ketone, diisobutyl ketone, methyl heptanone, cyclohexanone, trimethylcyclohexanone, isophorone, and acetophenone. The reactions between an activated hydrogen compound and an aldehyde or ketone are performed under the reaction conditions well known to those skilled in the art.

Compounds having two or more oxazolidine rings can be used as the blocked amine compounds, for example, the reaction product of N-hydroxyalkyl-oxazolidine and a polyisocyanate. N-hydroxyalkyl-oxazolidine is prepared in a

condensation reaction between an aldehyde, such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde or benzaldehyde, and a di(hydroxyalkyl)amine, such as diethanolamine or dipropanolamine. The polyisocyanate can be selected from, for example, the above-mentioned isocyanate compounds. A compound having two or more oxazolidine rings can be, for example, the product of the addition reaction between an N-hydroxyalkyl-oxazolidine and a diisocyanate, in a mole ratio of 2 to 1, respectively.

Compounds having two or more oxazolidine rings include an ester of an N-hydroxyalkyl-oxazolidine and a polycarboxylic acid. Polycarboxylic acids include, for example, oxalic acid, malonic acid, succinic acid, methylmalonic acid, isosuccinic acid, glutaric acid, adipic acid, itaconic acid, maleic acid, fumaric acid, phthalic acid, terephthalic acid, isophthalic acid, tetrachlorophthalic acid, mellitic acid and pyromellitic acid. Compounds having two or more oxazolidine rings can be obtained, for example, by esterification of two moles of N-hydroxyalkyl-oxazolidine and one mole of dicarboxylic acid, or by ester interchange with a dicarboxylic acid ester.

With respect to a compounding ratio of the above-described urethane prepolymer to the above-described blocked amine compound, it is desirable for the urethane resin composition to include 1 to 50 parts by weight of the blocked amine compound per 100 parts by weight of the urethane prepolymer. When the blocked amine compound is present at greater than 50 parts by weight per 100 parts by weight of urethane prepolymer, the resulting urethane resin composition is soft and has an inferior water resistance. On the other hand, when the blocked amine compound is present at less than one part by weight per 100 parts by weight of urethane prepolymer, film blistering is not prevented.

Inorganic fillers treated with an organic compound can be, for example, calcium carbonate treated with a fatty acid, such as lauric acid, stearic acid, palmitic acid, oleic acid or linoleic acid; calcium carbonate treated with a metal salt of a fatty acid, such as calcium palmitate, calcium stearate or sodium stearate; calcium carbonate treated with a fatty acid ester, such as stearyl stearate, lauryl stearate, methyl stearate, butyl stearate, steryl palmitate, lauryl palmitate or methyl laurate; calcium carbonate treated with a resin acid, such as calcium carbonate treated with rosin acid or abietic acid; calcium carbonate treated with a titanium compound, such as isopropyltriisostearoyl titanate; calcium carbonate treated with a silane, such as silane coupling agent; calcium carbonate treated with a surface active agent, such as alkyl benzene sulfonate; calcium carbonate treated with a poly(acrylic acid); and talc, bentonite and similar inorganic fillers, treated with an organic compound as described above.

Inorganic fillers treated with an organic compound which are available commercially include, for example, MC Coat S, M White, Snowlight SSS, EC Series, MS Series and Calfine Series of Maruo Calcium Co.; Raiton Series of Bihoku Funka Kogyo Co.; NCC Series and TSS Series of Nitto Funka Kogyo Co.; Gelton 50, SL-101, Hakuenka Series and Homocal Series of Shiraishi Kogyo Co. The inorganic filler treated with an organic compound is present in a urethane resin composition in an amount of at least 5 parts by weight, and preferably 10 parts by weight, per 100 parts by weight of the above-described urethane prepolymer. The inorganic filler treated with an organic compound is present in an amount of up to 400 parts, and preferably up to 250 parts, by weight per 100 parts by weight of the urethane prepolymer.

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top-coat was air-sprayed over the coated wall surface at a rate of 0.2 kg/m².

The waterproofing layers thus provided did not demonstrate any blistering, peeling, discoloration, cracking or water leakage two years after the application. The composition of Example 6 was a satisfactory waterproofing agent for walls.

EXAMPLE 10

A primer was coated on a roof of a concrete building at a rate of 0.2 kg/m². Three hours after priming, the urethane resin composition of Example 3 was applied with a roller at a rate of 0.3 kg/m², and immediately after that, a polyester unweaved fabric reinforcing material (50 g/m²) was applied over the coat of urethane resin. Five hours later, the condition of the urethane resin coat was such that an individual could stand on the coating. Then, the urethane resin composition of Example 3 was troweled at a rate of 1.5 kg/m². The next day an acrylic urethane top-coat was sprayed over the urethane resin composition.

The waterproofing layers thus provided did not demonstrate any blistering, peeling or water leakage one and one half years after application. The composition of Example 3 was a satisfactory waterproofing agent for roofs.

EXAMPLE 11

A primer was coated over a wall of a concrete building at a rate of 0.15 kg/m² with a brush. One hour after coating, a composition comprising 100 parts by weight of the urethane resin composition of Example 7, and 10 parts by weight xylol was air-sprayed over the coated wall surface at a rate of 1 kg/m². On the next day, an acrylic urethane top-coat was air sprayed over the coated wall surface at a rate of 0.2 kg/m².

The waterproofing layers thus obtained did not demonstrate any blistering, peeling, discoloration, cracking, or water leakage two years after application. The composition of Example 7 was a satisfactory waterproofing agent for walls.

What is claimed is:

1. A moisture-curable urethane resin composition comprising:

- (a) 100 parts by weight of a urethane prepolymer having two or more terminal isocyanate groups;
- (b) 6 to 50 parts by weight of a blocked amine compound having two or more oxazolidine rings which is essentially nonreactive with an isocyanate group and which

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generates a primary or a secondary amino group upon contact with moisture; and

- (c) 5 to 400 parts by weight of an inorganic filler treated with an organic compound selected from the group consisting of calcium carbonate treated with a fatty acid, calcium carbonate treated with a fatty acid metallic salt, calcium carbonate treated with a fatty acid ester, calcium carbonate treated with a resin acid, calcium carbonate treated with a titanium compound, calcium carbonate treated with a silane, calcium carbonate treated with a surface active agent, calcium carbonate treated with a polyacrylic acid, talc treated with a fatty acid, talc treated with a fatty acid metallic salt, talc treated with a fatty acid ester, talc treated with a resin acid, talc treated with a titanium compound, talc treated with a silane, talc treated with a surface active agent, talc treated with a polyacrylic acid, and mixtures thereof.

2. The moisture-curable urethane resin composition of claim 1 wherein the urethane prepolymer comprises a hydrophilic urethane prepolymer having a polyoxyalkylene chain including oxyethylene moieties.

3. The moisture-curable urethane resin composition of claim 2 wherein the oxyethylene moieties are present in the polyoxyalkylene chain in an amount of 5 weight percent or greater.

4. The moisture-curable urethane resin composition of claim 2 wherein the oxyethylene moieties are present in the polyoxyalkylene chain in an amount of 10 weight percent or greater.

5. The moisture-curable urethane resin composition of claim 1 wherein the hydrophilic urethane prepolymer has free isocyanate groups and is obtained from a reaction between (1) a polyoxyalkylene alcohol or a polyoxyalkylene polyol and (2) an organic polyisocyanate.

6. The moisture-curable urethane resin composition of claim 1 wherein the hydrophilic urethane prepolymer comprises a reaction product of an alcohol and a polyisocyanate.

7. The moisture-curable urethane resin composition of claim 1 wherein the urethane prepolymer is a compound having free isocyanate groups and is obtained from a reaction between a compound having two or more active hydrogens and a polyisocyanate.

8. The moisture-curable urethane resin composition of claim 1 wherein the urethane prepolymer comprises a polyisocyanate.

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United States Patent [19]

[11] 4,415,604

Nativi

Best Available Copy

[45] ~~Nov. 15, 1983~~

- [54] CONFORMAL COATING AND POTTING SYSTEM
- [75] Inventor: Larry A. Nativi, Rocky Hill, Conn.
- [73] Assignee: Loctite Corporation, Newington, Conn.
- [21] Appl. No.: 441,164
- [22] Filed: Nov. 12, 1982
- [51] Int. Cl.³ B05D 3/06
- [52] U.S. Cl. 427/54.1; 204/159.15; 204/159.19; 427/44; 525/455
- [58] Field of Search 427/54.1, 44; 204/159.16, 159.19, 159.15; 525/455
- [56] References Cited

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Primary Examiner—John H. Newsome
Attorney, Agent, or Firm—Hayes, Davis & Soloway

[57] ABSTRACT

Ultraviolet curable polymerizable coating system having a built-in secondary curing mechanism is disclosed. The polymerizable coating system is a one component system comprising at least one isocyanate-capped polyether diol and triol, an acrylate or methacrylate reactive diluent, and a polymerization initiator of the photoinitiator type. The coating system is also moisture curable.

18 Claims, No Drawings

resistance. However, diallyl phthalate varnishes require high temperature cure (approximately 150° C.) which severely limits their use. And, diallyl phthalate coatings and pottings also typically must be mechanically removed to permit repair.

The preceding discussion of background in the art of conformal coating circuit boards is taken largely from *Printed Circuits Handbook*, Clyde F. Coombs, Jr., Editor, McGraw Hill Book Company, Second Edition (1979).

As thus is apparent from the above discussion, none of the currently available conformal coatings and pottings are completely satisfactory since all prior art conformal coatings and pottings at best are a tradeoff of preferred application characteristics (i.e., processing speed, ease of application, pot life and cure conditions), preferred physical characteristics, (i.e., electrical properties, temperature, chemical and moisture resistance), and reparability.

It is thus a primary object of the present invention to provide an improved conformal coating and potting system, i.e. method and materials which overcomes the aforesaid and other disadvantages of the prior art.

Other objects of the present invention are to provide an improved composition for conformal coating printed circuit board assemblies and potting electrical and electronic components which compositions demonstrate extended pot life and ease of application, rapid dry-to-touch cure, good electrical properties, superior adhesion and abrasion resistance, excellent high temperature, chemical and moisture resistance, and ease of reparability. Yet other objects will in part appear obvious and will in part appear hereafter.

The invention accordingly comprises the process involving the several steps and relative order of one or more such steps with respect to each other, and the devices, materials and compositions possessing the features, properties and relations of elements which are exemplified in the following disclosure and scope of application of which will be indicated in the claims.

SUMMARY OF THE INVENTION

Generally, the foregoing and other objects of the invention are achieved by the provision of an ultraviolet (hereinafter "uv") curable polymerizable coating and potting system having a secondary cross-linking curing mechanism built in. More specifically, in accordance with the invention the polymerizable system is a one component coating system comprising (1) an isocyanate-capped prepolymer formed by reacting a blend of one or more polyether diols and one or more polyether triols with an excess of a diisocyanate, (2) a mono or polyfunctional acrylate or methacrylate reactive diluent, and (3) a polymerization initiator of the photoinitiator type. A particular feature and advantage of the instant invention is that the uv radiation cure produces extremely rapid dry-to-the-touch cure of all exposed areas of the coating or potting thereby permitting substantially immediate handling of the coated products and maintenance of the shape of the coating which might otherwise sag and creep, while secondary curing which occurs by moisture reaction of the isocyanate capped prepolymer provides substantially complete cure of unexposed (shadow) areas of the coating or potting under conditions of ambient temperature and humidity.

For a fuller understanding of the nature and objects of the present invention, reference should be made to

the following detailed description of the invention taken in connection with the accompanying examples.

The terms "liquid", and "solid" or "dry-to-the-touch" are used herein with reference to physical properties of the materials, are to be understood as to be referring to such properties as they exist under conditions as may be specified. For example, the term "liquid" refers to a physical state wherein a material is readily flowable while the terms "solid" and "dry-to-the-touch" are to be understood as referring respectively to physical states wherein a material is resistant to change in shape and is without free surface moisture or surface tackiness.

DETAILED DESCRIPTION OF THE INVENTION AND ITS PREFERRED EMBODIMENTS

The isocyanate-capped prepolymers employed in the coating system of the instant invention are formed by reacting a blend of one or more polyether diols and one or more polyether triols with an excess of at least one diisocyanate. The preferred polyether diols are selected from those having a molecular weight in the range of about 300 to about 5000, while the preferred polyether triols are selected from those having a molecular weight in the range of about 200 to about 3000. Particularly preferred is a blend of polyether diols having a molecular weight in the range of about 400 to about 1000, and polyester triols having a molecular weight of about 700.

The polyether diol/polyether triol blend typically comprises the polyether diol in substantial major proportion, e.g. seventy or more by weight of the polyether diol, while the polyether triol may be present in quite minor amount, e.g. as little as one to three percent of the polyether triol. The preferred diisocyanate is toluene diisocyanate (TDI) although other relatively low molecular weight diisocyanates of the general formula:



wherein R is a C₂₋₂₀alkylene, alkenylene or cycloalkylene radical or a C₆₋₄₀arylene, alkarylene or aralkylene are useful.

The polyether diol/polyether triol blend is reacted with excess diisocyanate. Generally the equivalent weight reaction ratio of the polyether diol/polyether triol blend to diisocyanate will be in the range of about 1.0 equivalent weights of polyether diol/polyether triol to about 1.6 to about 2.2 equivalent weight of diisocyanate. The preferred reaction ratio is 1.0 equivalents of the polyether diol/polyether triol blend for every 2.0 equivalents of diisocyanate. This preferred reaction ratio is particularly important to the properties of the final composition. The 2:1 ratio yields a final product with a chemical structure having a high degree of chemical, solvent and hydrolytic resistance.

At present the preferred prepolymer is based on a mixture of 0.916 equivalents of polyether diol (m.w. 1000 average) and 0.084 equivalents of polyether triol (m.w. 700 average) reacted with 2.0 equivalents of diphenylmethane diisocyanate (MDI). The resin resulting is then blended with an acrylate or methacrylate reactive diluent such as are exemplified by, but not limited to, trimethylol propane ethoxylate triacrylate, dicyclopentadiene methacrylate and dicyclopentadiene acrylate. Other reactive methacrylate compounds such as isobutyl methacrylate, isobornyl methacrylate, lauryl methacrylate and cyclohexylmethacrylate also can be beneficially utilized. The reaction preferably is accom-

plished in the absence of other i.e. non-reactive diluents.

The isocyanate-capped prepolymers typically comprise about 50 to about 75% by weight of the reaction mixture, and preferably will comprise about 65% by weight, while the acrylate or methacrylate reactant diluent typically will comprise about 25 to about 50% by weight of the reaction mixture, and preferably will comprise about 35% by weight.

The polymerization initiators useful in accordance with the present invention comprise ultra-violet (hereafter "uv") activated free-radical generators and typically may be employed in amounts of about 1% to about 10% by weight of the coating and potting composition. Many uv activated polymerization initiators are known in the art and may be advantageously employed in the invention. For example, the uv activated initiators may be selected from metal carbonyls of the formula $M_x(CO)_y$, wherein M is a metal atom, x is 1 or 2, and y is an integer determined by the total valence of the metal atoms, generally 4 to 10. The preferred uv activated initiators are selected from (a) C_{1-16} straight or branched chain alkyl diones; and (b) carbonyl compounds of the general formula $R^5(CO)R^6$ wherein R^5 is a C_{1-10} alkyl, aryl, aralkyl or alkaryl group, and R^6 is R^5 or hydrogen. In addition, R^5 or R^6 can contain any substituents which do not adversely affect the compound in serving its function. For example, R^5 or R^6 can be alpha-substituted with an alkyl, aryl, alkaryl, alkoxy or aryloxy radical, or with an amino or a mono- or dialkylamino derivative thereof, each of the above substituents containing up to about six carbon atoms. In addition, R^5 and R^6 taken together with carbonyl group form an aromatic or heterocyclic ketone containing up to about 16 carbon atoms.

It is useful, but not required to incorporate an adhesion promoter into the coating and potting system. The adhesion promoters may be chosen from any of those commonly known to the person reasonably skilled in the art. Two types of promoters are preferred. The first type consists of mono- and dicarboxylic acids which are capable of copolymerizing with the acrylate or methacrylate reactive diluent. The preferred species of these classes are methacrylic and acrylic acid. Such acids are used in proportions of 1-20% by weight of coating and potting system, preferable in proportion of 1-15%. The second preferred type of adhesion promoter is of the well-known silane type, present in the composition in proportions of 1-10% by weight of the coating and potting system.

Also optional, but recommended, are the inclusion of one or more chelators, cross-linking agents and/or polymerization inhibitors. Chelators and inhibitors are effective in amounts of about 0.1 to about 1% by weight of the coating and potting system. Ethylenediamine tetra-acetic acid and its sodium salt (Na_4EDTA), 1,1-ethylenebis-nitril methylidyne dipyridine and the class of beta-diketones are generally the most effective and are preferred. Cross-linking agents, optionally present in amounts from about zero to about 10% by weight of the coating and potting system, include such compounds as copolymerizable dimethacrylates.

The inhibitor concentration left over in the monomers from manufacture is often high enough for good stability. However, to insure maximum shelf life, the proportions mentioned above (about 0.1 to about 1% by weight of the coating and potting system) are recommended. Of those inhibitors which have been found of

adequate utility is the group consisting of hydroquinones, benzoquinones, naphthoquinones, phenanthraquinones, anthraquinones, and substituted compounds of any of the foregoing. Additionally, various phenols can be employed as inhibitors, the preferred one being 2,6-tert-butyl-4-methyl phenol.

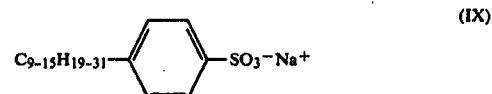
The amount of thickness, viscosity, or thixotropy desired can be varied in accordance with the particular application required. Thickeners, plasticizers, diluents, and various other reagents common to the art can be employed in any reasonable manner to produce the desired characteristics.

It is also optional, but recommended, that surfactants be present in the coating and potting system for optimum performance. Selection of suitable surfactants is a matter of simple experimentation. Obviously the surfactant must be soluble in the polymer composition and should be non-reactive with the isocyanate-capped prepolymer. The preferred surfactants are anionic materials such as the petroleum sulfonates having the formula:



wherein n is more than 20 and Me is a metal of valence x. Such materials are sold by, among others, Witco Chemical Corp., New York, N.Y., under the trademark "Alconate" 80, and by the Penreco Division of Penzoil, Butler, Pa., under the trademark "Petrobase."

Another suitable anionic type comprises the sodium alkyl or alkylaryl sulfonates having the formula:



Such materials are sold by E.I. duPont de Nemours & Co., Wilmington, Del., under the trademarks "Alkanol" 189-S and "DW" and the trademark "Duponol," and by Union Carbide Corp., New York, N.Y., under the trademark "Tergitol" (numerical series). Still another useful anionic class is the sulfonated ethoxylated types sold as the "Alipal" series by GAF Corp., New York, N.Y., and as "Neodol" 25-35 by Shell Chemical Co., Houston, Tex.

Surfactant concentration will depend in any given case upon the particular surfactant and reactive diluent being used. Optimization will be a matter of routine experimentation within the skill of the art. Ordinarily, however, minimum concentration of about 0.25 percent surfactant by weight of the coating and potting system will be needed to achieve an acceptable degree of emulsifiability, and a concentration of at least about 0.5 percent usually will be preferred. The maximum surfactant concentration will usually be about ten percent since above this level the surfactant may begin to interfere with the properties of the coating and potting system by adversely affecting, for example, its cure rate, stability or the cured products. As a practical matter, an upper concentration limit of about five percent, is usually satisfactory. For most surfactants or combinations of surfactants, the optimum concentration will probably fall in the range of about 1.0 to 2.5 percent by weight of the total coating and potting system.

The coating and potting system of the present invention is designed primarily as a uv curing product; however, due to the configuration of many circuit boards

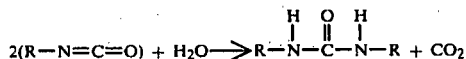
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and electrical and electronic components there are shadow areas that cannot be cured by uv light. To overcome this deficiency, a second curing mechanism has been built into the coating and potting system. More specifically, after exposure to uv a built-in moisture cure mechanism is available to complete curing of uncured areas of the coating and potting. The overall curing mechanisms are as follows:

(1) uv light polymerizes the acrylate or methacrylate species to provide fixture of the coating; and

(2) The isocyanate-capped prepolymer then reacts with water, specifically atmospheric moisture, i.e. according to the following formula.



This latter reaction provides ultimate physical properties and complete cure to the substrate.

EXAMPLE I

The invention will now be illustrated by the following description of a specific preferred embodiment thereof, given by way of example only. To a nitrogen-swept, four-necked resin kettle equipped with a stainless steel stirrer, nitrogen inlet tube, thermometer, condenser, and entrance port, add 286 grams of Upjohn LF-168 diphenylmethane diisocyanate (MDI). Then slowly add at 60° with mixing 466 grams of polyether diol (100 m.w. average) and 20 grams of polyether triol (700 m.w. average). Heat to 60° C. with mixing for one hour and then at 90° C. for one and one half hours. Cool to room temperature, add 260 grams of trimethylol propane ethoxylate triacrylate and 30 grams of Ciba-Geigy Irgacure 651 dimethoxy-2-phenyl acetophenone, and blend.

The resulting blend was applied by dipping the back side surface of an audio speaker cone. Cure of the coating was effected by exposing the speaker to uv radiation (3650 angstroms, 60,000 microwatts per square centimeter) for 20 seconds. Those areas of the coating exposed to uv radiation were solid and dry to the touch within 25 to 45 seconds. Shadow areas of the speaker core, i.e. not receiving direct uv radiation, were wet to the touch initially, but were found to be fully cured after standing at ambient temperature and humidity conditions for twenty-four hours. The speaker core was sliced through shadow areas, and the coating was found to be fully cured to the board surface after twenty-four hours.

The coating was humidity tested as follows: The coated speaker cone was placed on a rack in a stainless steel tank, and 500 grams of water added to the bottom of the tank. The tank was closed, sealed, and heated to a temperature of 115° C. After heating for 40 hours, the tank was allowed to cool. The tank was then opened, and the cone removed and examined. No visible blistering or other evidence of coating failure was observed.

EXAMPLE II

The procedure of Example I was repeated except 260 grams of dicyclopentenyl methacrylate was employed in place of the trimethylol propane ethoxylate triacrylate. Similar results to Example I were obtained.

EXAMPLE III

The procedure of Example II was repeated except 260 grams of dicyclopentadiene acrylate was employed

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in place of the trimethylol propane ethoxylate triacrylate. Similar results to Example I were obtained.

As will be appreciated the foregoing invention provides novel and improved coating systems for conformal coating and potting printing circuit boards and electrical and electronic components and the like. The coating and potting systems may be applied to the circuit board substrates or components by any convenient manner, for instance, by brushing, dripping, rolling, dipping, etc. or by spraying (when suitably diluted). Moreover, the coating and potting systems cure through dual mechanisms including uv cure which permits fast fixture cure thereby achieving almost immediate dry-to-the-touch curing. However, unlike conventional uv cured products, the coating and potting systems of the present invention do not require full area irradiation to achieve full cure due to their built-in secondary cure mechanism. Moreover, the cured coatings and pottings have excellent adherence to plastics, metal, glass and wood, good abrasion resistance, and are hydrolytically stable and resistant to thermal cycling. The coating and pottings also are repairable, i.e., can be removed by selective solvents such as methyl ethyl ketone, and then replaced by brush or spray, and uv cured.

The invention has been described particularly with application to potting audio speaker cores. However, one skilled in the art would appreciate that the coating and potting systems may be applied to other electrical electronic components such as printed circuit board assemblies, electrical transformers or the like. Moreover, the coating and potting system is not limited to the use in the electronics field but may be employed in any industrial area where conformal protective coating and/or potting is desired.

I claim:

1. A one-part coating composition, especially useful for conformal coating and potting, comprising:

- (1) At least one isocyanate-capped polyether diol and triol;
- (2) An acrylate or methacrylate reactive diluent; and
- (3) A polymerization initiator of the photo-initiator type.

2. The coating and potting composition of claim 1, wherein said isocyanate-capped polyether diol and triol comprises the reaction product of a blend of at least one polyether diol and at least one polyether triol with excess diisocyanate.

3. The coating and potting composition of claim 2, where the polyether diol portion comprises a polyether diol of molecular weight in the range of about 300 to about 5,000 average.

4. The coating composition of claim 2, wherein the polyether triol portion comprises a polyether triol of molecular weight in the range of about 200 to about 3,000 average.

5. The coating and potting composition of claim 2, where said polyether diol has a molecular weight of about 400 to about 1,000 average, and said polyether triol has a molecular weight of about 700 average.

6. The coating and potting composition of claim 2, where said polyether diol and polyether triol blend comprises said polyether diol in major proportion.

7. The coating and potting composition of claim 2, where said isocyanate-capped polyether diol and triol comprises the reaction product about 1.0 equivalents of said polyether diol and polyether triol blend with about 1.6 to about 2.2 equivalents of diisocyanate.