

(CONVENTION. By one or more persons and/or a Company.)

636610

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address(es).

X We ⁽¹⁾ ALTOSUN PTY. LTD.
of Level 46, 19-29 Martin Place, Sydney, New South Wales,
..... Australia

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: ⁽²⁾
..... CHEMICALLY-CURING, TWO-PART POLYURETHANE COMPOSITIONS

(3) Here insert number(s) of basic application(s).

which is described in the accompanying complete specification. This applications is a Covention application and is based on the application numbered ⁽³⁾
..... 8911669.3

(4) Here insert Name of basic Country or Countries, and basic date or dates.

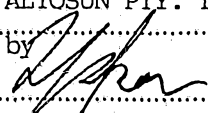
for a patent or similar protection made in ⁽⁴⁾ United Kingdom
..... on 20th May 1989

MX Our address for service is WATERMARK PATENT & TRADEMARK ATTORNEYS
290 Burwood Road, Hawthorn, Victoria, Australia.

DATED this 20th day of May 19 90 ..

(5) Signature(s) of Applicant(s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association.

FO 23/05/90

(5) ALTOSUN PTY. LTD.
by 
..... L. J. Dyson
..... Registered Patent Attorney

To: THE COMMISSIONER OF PATENTS.

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

(1) Here insert (in full) Name of Company.

In support of the Convention Application made by⁽¹⁾.....

ALTOSUN PTY. LTD

(hereinafter referred to as the applicant) for a Patent

(2) Here insert title of Invention.

for an invention entitled:⁽²⁾ "Chemically-curing,

two-part polyurethane compositions"

(3) Here insert full Name and Address, of Company official authorized to make declaration.

I,⁽³⁾ WILLIAM BOLEDZIUK

of ~~ALTOSUN PTY. LTD. T/AS BOSTIK 3 Cliff Street, Essendon 3040, Australia.~~
~~51 HIGH STREET, THOMASTOWN, VICTORIA, 3074~~

do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in⁽⁴⁾ United Kingdom

(4) Here insert basic Country or Country of Origin followed by date or dates and basic Applicant or Applicants.

on the 20th day of May 1989, by BOSTIK LIMITED

on the day of 19....., by

(5) Here insert (in full) Name and Address of Actual Inventor or Inventors.

3.⁽⁵⁾ Gerhard PIESTERT, Ahornweg 11, D-6870 Schwetzingen and Wolfgang Haar, Berliner Strasse 40, D-6370 Oberursel both of Federal Republic of Germany

xs/are the actual inventor of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of Gerhard Piestert and Wolfgang Haar by virtue of an assignment to Bostik Limited dated 6 June 1989 and an assignment dated 23rd March 1990 from Bostik Limited to Altosun Pty. Ltd.

4. The basic application referred to in paragraph 2 of this Declaration was.....the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Thomastown Victoria 3074

this 5th



AU9055774

(12) PATENT ABRIDGMENT (11) Document No. AU-B-55774/90
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 636610

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CHEMICALLY-CURING, TWO-PART POLYURETHANE COMPOSITIONS
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- (71) Applicant(s)
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- (72) Inventor(s)
GERHARD PIESTERT; WOLFGANG HAAR
- (74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122
- (56) Prior Art Documents
AU 55775/90 C08G 18/10 18/32 C09D 175/04
US 4341689
FR 2303844
- (57) Claim

1. A chemically-curing two-part polyurethane composition comprising Part A which comprises a prepolymer with terminal isocyanate groups and which is mixed with Part B which comprises water or a water-containing composition characterised in that Part A is filled with a molecular sieve free from adsorbed water and loaded with a primary or secondary amine with 2 or more functionalities.

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Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

Class

Int. Class

Application Number:

Lodged:

Complete Specification Lodged:

Accepted:

Published:

Priority :

Related Art :

Name of Applicant : ALTOSUN PTY. LTD.

Address of Applicant : Level 46, 19-29 Martin Place, Sydney, New South Wales, Australia

Actual Inventor : GERHARD PIESTERT and WOLFGANG HAAR

Address for Service : WATERMARK PATENT & TRADEMARK ATTORNEYS.
LOCKED BAG NO. 5, HAWTHORN, VICTORIA 3122, AUSTRALIA

Complete Specification for the invention entitled:

CHEMICALLY-CURING, TWO-PART POLYURETHANE COMPOSITIONS

The following statement is a full description of this invention, including the best method of performing it known to :-

US

CHEMICALLY-CURING, TWO-PART
POLYURETHANE COMPOSITIONS

5 The present invention relates to chemically-curing, two-part polyurethane compositions which can be used as adhesive, sealant, moulding or coating compositions.

Such two-part polyurethane compositions comprise Part A which comprises a prepolymer with terminal
10 isocyanate groups and which is mixed with Part B which comprises water or a water-containing composition.

Two-part polyurethane adhesive and sealant compositions are well-known in which Part A contains isocyanate and Part B contains polyol or polyamine. In
15 order to obtain a satisfactorily uniform reaction product it is necessary to use stoichiometrical amounts of Part A and Part B which must be precisely measured and then mixed homogeneously. Additionally, the moisture content of these
20 compositions must be carefully controlled, and the rate of cure limited, since too high water content leads to foaming of the mixture due to reaction of isocyanate with the water, often leading to CO₂ blistering. Effective production and application of these conventional two-part
25 polyurethane compositions often requires complex and expensive metering and mixing equipment.

It is an object of the present invention to provide a two-part polyurethane composition which can be cured at a reasonably fast rate without CO₂ blister formation.

30 It is another object of the invention to provide a satisfactory polyurethane composition which does not require close adherence to stoichiometric proportions.

According to the present invention, we provide a chemically-curing two-part polyurethane composition
35 comprising Part A which comprises a prepolymer with terminal isocyanate groups and which is mixed with Part B

which comprises water or a water-containing composition characterised in that Part A is filled with a molecular sieve free from adsorbed water and loaded with a primary or secondary amine with 2 or more functionalities.

5 When mixing of Parts A and B brings water into contact with Part A, rapid desorption of the polyamine takes place which can then react rapidly with the isocyanate groups.

10 The molecular sieve used in the present invention may be loaded with up to 25 wt% of amine and it is preferred to load the amine to at least 50% and preferably 75% of the capacity of the molecular sieve. Up to 90% of the capacity of the molecular sieve could be amine-loaded without showing storage stability problems. The
15 polyurethane compositions of the invention show remarkable stability, both at room temperature and at elevated temperatures. Indeed, curing of Part A by thermal desorption does not take place; after heating to 120°C for four hours, no increase in viscosity is observed.

20 The present invention provides a two-part polyurethane composition which quickly cures to an acceptable product, with a high degree of uniformity without requiring accurate metering in stoichiometric proportions and homogeneous mixing. The system thus
25 provided needs only very simple mixing and application equipment.

 Perhaps surprisingly, it is also found that water can be added to a Part A according to the invention in substantial excess and with incomplete (not homogeneous)
30 mixing and yet the mixture still cures rapidly to a CO₂ blister-free product.

 It was known to use molecular sieves loaded with various reactive materials, including amines as well as peroxides, hydrogensulphides etc., as reactive components
35 of e.g. lacquer systems or rubber components. Amine-loaded molecular sieves have also been used as secondary

accelerators in neoprene, polyacrylonitrile and polybutadiene formulations. However, the amines in these cases are tertiary amines. Furthermore, commercially available amine-loaded molecular sieves have not been found
5 suitable for use in the present invention since the resulting blends have been found not to be stable at elevated temperature. It is thought that this may possibly be due to the fact that these commercial amine-loaded molecular sieves may contain significant amounts of water
10 which could interfere with the reaction and weaken the adsorption of the amine.

As has been said, accurate metering and mixing of Part A and Part B is no longer necessary in the present invention. This greatly simplifies the application of the
15 compositions, Part B may be applied either in excess - without foaming or formation of CO₂ blisters - or in less than stoichiometric proportions - when ambient humidity completes the cure. Indeed, in certain circumstances, Part
A may be applied alone and allowed to cure with ambient
20 moisture from the air or from the substrate to be bonded. This may be done, for example, to purge a mixer at the end of an application.

The pot life of such compounds may be varied within certain limits by the amount of water added and the
25 quality of the mixture. If for example mixing is performed very carefully, the composition may be cured after only 5 minutes. On the other hand, if mixing is performed less thoroughly, pot life may be 15 minutes or longer.

Two-part polyurethane compounds according to this
30 invention also permit the use of high concentrations of isocyanate in Part A, a pre-requisite in many applications in order to obtain satisfactory adhesive and cohesive properties.

In addition, the use of amine-loaded molecular
35 sieves allows combination with aliphatic isocyanates which are of low reactivity and which, even in the presence of

suitable catalysts, react only slowly with water, but rapidly enough with polyamines. Formulations without or with low concentrations of catalyst reveal better hydrolytic and thermal stability.

5 The isocyanate-terminated prepolymers of Part A may be derived from polyols such as polyester polyols, polyether polyols, polybutadiene polyols, polyacrylate polyols, polyisoprene polyols and others. The polyols are reacted with excess isocyanate, leading to terminal
10 isocyanate groups which are available for further reactions. Representative examples of isocyanates are 2.4- or 2.6 tolylene diisocyanate (TDI), 4.4'-diphenylene methane diisocyanate (MDI), 4.4'-dicyclohexyl, methane diisocyanate (HMDI), isophorone diisocyanate (IPDI) etc.

15 Molecular sieves of pore sizes 4 Å ^{to} ~~and~~ 5 Å have been effective in all tests.

 Representative examples of polyamine to be absorbed on the molecular sieves are ethylene diamine, propylene diamine, diethylene triamine, triethylene
20 tetramine, etc.

 In order that the invention may be better understood preferred Examples will now be described in greater detail.

25 EXAMPLES

A. Preparation of amine-loaded molecular sieve

(a) 3g ethylene diamine were added to 20g molecular sieve (4Å) in 50g dry 'Mesamoll' - alkyl sulphonic acid ester of
30 phenol - (Registered Trade Mark - Bayer) (corresponding to approx. 75% saturation). After 10 days the free amine remaining in the 'Mesamoll' was determined. This indicated that 98.7% of the polyamine was adsorbed.

35 (b) 3.6g ethylene diamine were added to 20g molecular sieve (5Å) in 50g dry 'Mesamoll' (corresponding to approx.



90% saturation). After 2 weeks the free amine remaining in the 'Mesamoll' was determined. This indicates that 98.3% of the polyamine was adsorbed.

5 It is not necessary to separate the thus-loaded molecular sieves from the 'Mesamoll'; the suspensions may be used as such in the preparation of the polyurethane compositions.

10 B. Formulation with prepolymer

EXAMPLE 1

Preparation of Part A (1)

25g 'Mesamoll' and 15.0g MDI were added to 18.25g of the
15 suspension from (a). The mixture was stirred vigorously for 10 minutes. Then 100g 'Desmophen' 1900 U - polyether diol of polypropylene oxide (equivalent weight about 1000) - (Registered Trade Mark - Bayer) and 0,1% dibutyltin dilaurate were added and the mixture kept at 80°C for 2
20 hours. The isocyanate content of the resulting prepolymer was 21 mVal.

Production of polyurethane

Pure water was used as Part B(1).

25 After mixing 10g water (50 times the stoichiometric amount) into the above Part A(1) formulation, the product cured within approx. 10 minutes without CO₂ blister formation.

In comparison, curing of a similar composition without the amine-loaded molecular sieve took more than two
30 hours and produced severe foaming.

EXAMPLE 2

Preparation of Part A (2)

15.62g MDI were added to 29.44g of suspension (b) and
35 13.81g 'Mesamoll'. The mixture was stirred vigorously for 10 minutes. Then 100g 'Desmophen' 1910 U - polyether triol

of polypropylene oxide - (equivalent weight about 1300) - and 0.1% dibutyltin dilaurate were added and the mixture kept at 80°C for 2 hours. The isocyanate content of the resulting prepolymer was 44 mVal.

5

Production of polyurethane

Pure water was again used as Part B(2)

After mixing 20g water (50 times the stoichiometric amount) into the above Part A(2) formulation, the product cured within approx. 10 minutes without CO₂ blister formation.

10

EXAMPLE 3

Preparation of Part A(3)

Part A(3) was prepared as described in EXAMPLE 2 above.

15

Preparation of Part B(3)

A waterpaste was prepared by dispersing 15g water and 3g 'Aerosil' 200 (Registered Trade Mark - Degussa) in 70g 'Mesamoll' and the dispersion thoroughly mixed during addition of 15g carbon black.

20

Production of polyurethane

5.3g of the Part B(3) (i.e. twice the stoichiometre amount) was mixed with the part A(3), using a ten-element static mixer. The mixture gelled within 5 minutes, without CO₂ blister formation, and was fully cured after about 60 minutes.

25

A comparative composition prepared using a Part A without the amine-loaded molecular sieve together with Part B(3) when mixed by a ten element static mixer resulted only in a foaming mixture.

30

EXAMPLE 4

Part A(4) was also prepared as described in EXAMPLE 2 above and Part B(4) was prepared as described in Example 3 above.

35

Production of polyurethane

2g of Part B(4) (75% of the stoichiometre amount) was mixed with the Part A(4) prepared as described in EXAMPLE 2, again using a ten-element static mixer. The
5 resulting mixture gelled after 20 minutes, and there was no foaming or CO₂ blister formation. Full cure, with the aid of ambient moisture, was achieved within one day.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

~~Claims~~

5 1. A chemically-curing two-part polyurethane composition comprising Part A which comprises a prepolymer with terminal isocyanate groups and which is mixed with Part B which comprises water or a water-containing composition characterised in that Part A is filled with a molecular sieve free from adsorbed water and loaded with a primary or secondary amine with 2 or more functionalities.

10

2. A two-part polyurethane composition according to claim 1 wherein the molecular sieve may be loaded with up to 25 wt% of amine.

15

3. A two-part polyurethane composition according to claim 2 wherein the molecular sieve is loaded with amine to at least 50% and preferably 75% of its capacity.

20

4. A two-part polyurethane composition according to any one of claims 1 to 3 which will cure without CO₂ blister formation even when mixing of Parts A and B is not fully homogeneous.

25

5. A two-part polyurethane composition according to any one of the preceding claims wherein the pores of the molecular sieve are 4Å to 5Å.

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6. A two-part polyurethane composition according to any one of the preceding claims wherein Part A and Part B are mixed in non-stoichiometric proportions.

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7. A chemically-curing two-part polyurethane composition substantially as hereinbefore described with reference to and as illustrated by the Examples.

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DATED this 17th day of May 1990.

ALTOSUN PTY. LTD.

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