(CONVENTION. By one or more persons and/or a Company) Form 3

631794

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).

XI/We (1) DOW CORNING LIMITED

of Inveresk House, 1 Aldwych, London WC2R 0HF, England

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2) N-CONTAINING ORGANOSILICON COMPOUNDS

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

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered (3) 8811601.7 & 8902939.1

(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 17th May 1988 and 9th February 1989

xxMy/Our address for service is ~~Messrs Edward Waters & Sons, Patent Attorneys,~~ Watermark Patent & Trademark Attorneys, 50 Queen Street, Melbourne, Victoria, Australia.

M 009025 160589

DATED this 15th day of May 19 89

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

(5)

DOW CORNING LIMITED

by

Ian A. Scott

Registered Patent Attorney

AUSTRALIAN PATENT OFFICE

To:

(CONVENTION. Company.) Form 8

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) DOW CORNING LIMITED of Inveresk House, 1 Aldwych, London WC2R OHF

(hereinafter referred to as the applicant) for a Patent

(2) Here insert title of Invention.

for an invention entitled:(2) ORGANOSILICON COMPOUNDS

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

I,(3) ALAIN F. JOACHIM, Director

of 154 Chaussee de la Hulpe, 1170 Brussels, Belgium

do solemnly and sincerely declare as follows:

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

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

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

on the 17th day of May 19 88, by DOW CORNING LIMITED

on the 9th day of February 1989, by DOW CORNING LIMITED

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

3.(5) STEPHEN EDWARD CRAY, JAMES MCVIE and PAUL ANTONY YIANNI of 10 Doniford Close, Sully, South Glamorgan, Wales, U.K., 12 St. Brannocks Close, Barry, South Glamorgan, Wales, U.K. and Clos de Spervenches 7, 1350 Limal, Belgium

is/~~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 the said actual inventors

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

DECLARED at Brussels, Belgium

this 25th day of May 19 89

(6) Signature.

(6) Alain Joachim

ALAIN F. JOACHIM - DIRECTOR

To: THE COMMISSIONER OF PATENTS.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-34777/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 631794

(54) Title
N-CONTAINING ORGANOSILICON COMPOUNDS

International Patent Classification(s)
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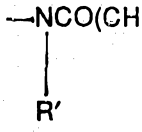
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

(56) Prior Art Documents
EP 363071
AU 577998 50622/85 C08G 77/26 77/04 C07F 7/04
EP 54426

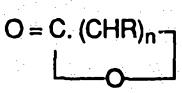
(57) Claim

1. An organosilane compound according to the general formula $R^1_aA_bSi(R''\text{-}NR'\text{-}X)_c$ wherein A represents a hydroxyl or a hydrolysable group, R^1 represents a monovalent hydrocarbon group having up to 8 carbon atoms, R′ represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkenyl group or an aryl group, or a group X, R″ represents a divalent hydrocarbon group which may have nitrogen, oxygen or sulphur present in the carbon chain, X represents a group $CO(CHR)_nOH$ in which R represents a hydrogen atom or an alkyl group, a has the value 0, 1, or 2, b has the value 1, 2, or 3, c has the value 1 or 2, the sum of a + b + c = 4 and n has a value in the range 2 to 7.

4. A method for the preparation of an organosilane compound having a group



the organosilicon compound through a divalent hydrocarbon group which may have nitrogen, oxygen or sulphur atoms present in the chain wherein R′ is as defined in claim 1, R represents a hydrogen atom or an alkyl group and n has a value in the range 2 to 7 which method comprises heating together under reflux conditions a lactone of the general formula



.../2

and an amino substituted organosilane compound according to the general formula $R^1_aA_bSi(R''NR^4\text{-}H)_c$ wherein A represents a hydrolysable group, R^1 represents a monovalent hydrocarbon group having up to 8 carbon atoms, R^4 represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkenyl group or an aryl group, R'' represents a divalent hydrocarbon group which may have nitrogen, oxygen or sulphur present in the carbon chain, a has the value 0, 1, or 2, b has the value 1, 2, or 3, c has the value 1 or 2, the sum of a + b + c = 4.

10. An organosilane compound prepared by a method according to Claim 4.

631794

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 : DOW CORNING LIMITED

Address of Applicant : Inveresk House, 1 Aldwych, London WC2R OHF
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Address for Service : EDWD. WATERS & SONS, Watermark Patent & Trademark Attorneys
50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

N-CONTAINING
ORGANOSILICON COMPOUNDS

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

N-CONTAINING ORGANOSILANE COMPOUNDS

This invention is concerned with N-containing organosilane compounds.

Organosilanes are known which have substituent groups including amido groups. It has been proposed to prepare silanes having substituents which include a distally extending tail of monohydroxysubstituted carbon atoms linked to the silicon atom through an amido group, by reaction between the corresponding amino silane and an aldonic acid lactone, as exemplified by delta gluconolactone. These materials have a plurality of hydroxyl groups in the substituent. They are water soluble and are said to cure to a hard clear insoluble protective coating on certain substrates. These characteristics are undesirable for some applications; furthermore we have found such materials are prepared with difficulty.

The present invention provides in one of its aspects an organosilane compound according to the formula $R^1{}_aA_bSi(R''\text{-}NR'\text{-}X)_c$ in which A represents a hydroxyl or a hydrolysable group, R^1 represents a monovalent hydrocarbon group having up to 8 carbon atoms, R′ represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkenyl group or an aryl group, or a group X, R″ represents a divalent hydrocarbon group which may have nitrogen, oxygen or sulphur present in the carbon chain, X represents the group $CO(CHR)_nOH$, a has the value 0, 1 or 2, b has the value 1, 2 or 3, c has the value 1 or 2, the sum of a + b + c = 4.

Organosilane compounds according to the invention are materials in which the group $-NCO(CHR)_nOH$ is part of a substituent wherein one of the nitrogen valencies is

$$\begin{array}{l} -N- \\ \quad | \\ \quad R' \end{array}$$

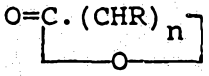
linked to the silicon atom through a divalent linkage R″.

Preferably R represents a hydrogen atom and n has the value 3, 4, 5 or 6. Preferred materials are those wherein R" represents a divalent hydrocarbon group or a group $R'"(NR'R"')_s$ wherein R"' represents a divalent hydrocarbon group, R' is as referred to above and s has a value in the range 0 to 4, more preferably 1 or 2. Preferred groups R"-NR'-X according to the general formula

$$-R"'-\underset{\displaystyle R'}{\overset{\displaystyle |}{N}}-R"'-NR'-(C=O)-(CHR)_n-OH$$

in which R"'is selected from the groups $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$ and $-CH_2CH(CH_3)CH_2-$, and R' represents a hydrogen atom. The hydrolysable groups A of the silane may be selected for example, from alkoxy, (e.g. methoxy, ethoxy or propoxy) alkoxyalkoxy (e.g. methoxy-ethoxy) acetoxy and halogen (e.g. chlorine). The silanes are hydrolysable materials and may be employed as end-blocking units for polysiloxanes, or as chain extending or chain branching agents depending on the values of a and b. They may be hydrolysed to provide a polysiloxane with or without the presence of other silanes, for example to provide a polysiloxane, or condensed with for example polysiloxanes having having hydroxyl or other reactive groups, for example linear α,w dihydroxypolysiloxanes, to provide a polysiloxane.

Organosilane compounds of the present invention may be prepared by reaction between a lactone and an organosilane compound having an amino substituent. Suitable lactones have the formula



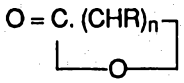
in which R represents a hydrogen atom or a hydrocarbon group having for example up to 7 carbon atoms, such as may be present when the lactone has been derived from a gamma hydroxy acid and n has a value in the range 2 to 7.

Preferred lactones are those in which each R represents a hydrogen atom and n has the value 3, 4, 5 or 6, for example gamma butyrolactone and epsilon caprolactone. Various amino substituted organosilicon compounds are known and available and they can be made by methods known in the art. The amino substituted organosilane compound may be a silane according to the general formula $R^1_aA_bSi(R''NH\text{-}R^4)_c$ wherein A represents a hydroxyl group or a hydrolysable group, R^1 represents a monovalent hydrocarbon group having up to 8 carbon atoms, R^4 represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkenyl group or an aryl group, R'' represents a divalent hydrocarbon group which may have nitrogen, oxygen or sulphur present in the carbon chain, a has the value 0, 1, or 2, b has the value 1, 2, or 3, c has the value 1 or 2, the sum of a + b + c = 4. The hydrolysable aminosilane may have hydrolysable groups selected for example, from alkoxy, alkoxyalkoxy, acetoxy and chloro. The alkoxy silanes are generally preferred. As mentioned above, examples of suitable groups R''' include $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$ and $-CH_2CH(CH_3)CH_2-$. Operative amino containing substituents $R''NR^4H$ include $-(CH_2)_3NH_2$, $-(CH_2)_3-NHCH_2CH_2NH_2$, $-CH_2CH(CH_3)-CH_2NHCH_2CH_2NH_2$, and $-(CH_2)_3-NHCH_2CH_2NHCH_2CH_2NH_2$.

The organosilane compounds of the invention may be made by any convenient method, for example, by modification of some or all of the amino groups of the appropriate aminosilane. Silanes produced may be subsequently hydrolysed or condensed e.g. with a siloxane or polysiloxane or other silane in known manner, e.g. by emulsion polymerisation, to provide a polysiloxane. If desired the condensation step may be followed by equilibration and separation in known manner. Reaction between the lactone and the amino substituted organosilane compound to form the amide may be carried out under a variety of conditions and is preferably carried out by heating the reactants together, optionally for example in aqueous emulsion or in solution, most preferably under reflux in, for example, methyl ethyl ketone, toluene or ethanol. The proportions of the reactants employed may be chosen so that the desired proportion of the amino groups of the amino substituted organosilane compound are converted to the amido form. For example one may ensure that from 20 to 80% of the primary amino groups are modified by reaction with the lactone.

The invention provides in another of its aspects a method for the preparation of an organosilicon compound having a group $-\underset{\displaystyle R'}{\overset{\displaystyle |}{N}}CO(CHR)_nOH$

wherein one of the nitrogen valencies is connected with a silicon atom of the organosilicon compound through a divalent hydrocarbon group which may have nitrogen, oxygen or sulphur atoms present in the chain wherein R represents a hydrogen atom or an alkyl group and n has a value in the range 2 to 7 which method comprises heating together under reflux conditions a lactone of the general formula



and an amino substituted organosilicon compound which comprises a silane according to the general formula $R^1_aA_bSi(R''NR^4\text{-}H)_c$ wherein A represents a hydroxyl or a hydrolysable group, R^1 represents a monovalent hydrocarbon group having up to 8 carbon atoms, R^4 represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkenyl group or an aryl group, R'' represents a divalent hydrocarbon group which may have nitrogen, oxygen or sulphur present in the carbon chain, a has the value 0, 1, or 2, b has the value 1, 2, or 3, c has the value 1 or 2, the sum of a + b + c = 4.

Organosilicone compounds which are prepared from silanes according to the general formula $R^1_aA_bSi(R''NR^4\text{-}H)_c$ wherein R^1, A, R'' R^4 and the values of a, b and c are as aforesaid final use in a variety of applications for example as coatings or finishes on various substrates. They may be formulated for example, as solutions or emulsions and may be formulated so as to become cured on the substrate to which they have been applied. For example, they may be employed as a blend with other ingredients for example polydimethylsiloxanes or with materials commonly employed in coatings or finishes. The organosilicon compounds are efficacious in the treatment of fibres and particularly natural fibres, for example new or freshly laundered textile fabrics consisting of or incorporating fibres of cotton, which may be blended with other fibres, for example polyester, to provide a finish which confers a good handle or feeling of softness and a less yellow colouring to the fabric than similar treatments with the corresponding polysiloxane having solely amino organofunctionality. Those polysiloxanes having both amido siloxane units as specified and primary amino substituted siloxane units may be used for the treatment of fibres and particularly natural fibres, for example textile fabrics incorporating fibres of cotton, to provide a finish which shows a desirable blend of softness, whiteness and durability. The preparation of organosilicon compounds of the invention from the appropriate lactone and organosilane is particularly beneficial as no undesirable by-product is released during the reaction.

In order that the invention may become more clear there now follows a description of example organosilicon compounds which are illustrative of the invention. In the Examples all parts and percentages are expressed by weight unless otherwise specified, and Me signifies the methyl group.

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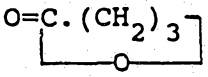
Example 1

Example silanes 1, 2, and 3 according to the invention were made as follows. Silane 1 was prepared thus: 1.63 moles of the silane $Me.(MeO)_2SiQ$ in which Q represents the group $CH_2.CHMe.CH_2.NH.(CH_2)_2NH_2$ were charged to a split-necked flask fitted with reflux condenser, stirrer and thermometer. 1.63 moles gamma butyrolactone



were added dropwise to the silane in the flask and the mixture stirred and heated to 80°C. The reacting mixture was maintained at this temperature under a blanket of nitrogen for five hours. The mixture was allowed to cool in the flask. The product was a viscous yellow liquid having a viscosity at 25°C of 129,600 mm^2/s of the formula

$$Me.(MeO)_2SiCH_2.CHMe.CH_2.NH.(CH_2)_2NHCO(CH_2)_3OH.$$

Silane 2 was prepared in the same manner as Silane 1 except that the group Q of the aminosilane employed was $(CH_2)_3.NH.(CH_2)_2NH_2$. Silane 2 had a viscosity of 38,000 mm^2/s at 25°C. Silane 3 was prepared in similar fashion to Silane 1 except that the silane $(MeO)_3SiQ$ in which Q represents the group $CH_2.CHMe.CH_2.NH.(CH_2)_2NH_2$ was used as starting material. Silane 3 was a viscous yellow liquid having a viscosity of 43,280 mm^2/s at 25°C .

2 moles of Silane 1 was mixed with 1 mole of α,w dihydroxypolydimethyl siloxanes having a viscosity of 150 mm^2/s, heated to 50°C for four hours and then cooled to room temperature. An aqueous emulsion was prepared using this product together with an ethoxy based surfactant. The emulsion was padded onto a cotton fabric such that about 0.7% silicone solids was present on the weight of the fabric. The fabric was found to exhibit non-yellowing characteristics and to confer a soft handle to the fabric.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

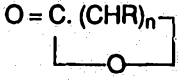
1. An organosilane compound according to the general formula $R^1_aA_bSi(R''\text{-}NR'\text{-}X)_c$ wherein A represents a hydroxyl or a hydrolysable group, R^1 represents a monovalent hydrocarbon group having up to 8 carbon atoms, R' represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkenyl group or an aryl group, or a group X, R'' represents a divalent hydrocarbon group which may have nitrogen, oxygen or sulphur present in the carbon chain, X represents a group $CO(CHR)_nOH$ in which R represents a hydrogen atom or an alkyl group, a has the value 0, 1, or 2, b has the value 1, 2, or 3, c has the value 1 or 2, the sum of a + b + c = 4 and n has a value in the range 2 to 7.

2. An organosilane compound according to Claim 1 wherein R'' represents $R'''(NR'R''')_s$ wherein R''' represents a divalent hydrocarbon group and s has a value in the range 0 to 4.

3. An organosilane compound according to Claim 2 wherein R''' is selected from the groups $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$ and $-CH_2CH(CH_3)CH_2-$.

4. A method for the preparation of an organosilane compound having a group $-NCO(CHR)_nOH$ wherein one of the nitrogen valencies is connected with a silicon atom of

the organosilicon compound through a divalent hydrocarbon group which may have nitrogen, oxygen or sulphur atoms present in the chain wherein R' is as defined in claim 1, R represents a hydrogen atom or an alkyl group and n has a value in the range 2 to 7 which method comprises heating together under reflux conditions a lactone of the general formula



and an amino substituted organosilane compound according to the general formula $R^1_aA_bSi(R''NR^4\text{-}H)_c$ wherein A represents a hydrolysable group, R^1 represents a monovalent hydrocarbon group having up to 8 carbon atoms, R^4 represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkenyl group or an aryl group, R''

represents a divalent hydrocarbon group which may have nitrogen, oxygen or sulphur present in the carbon chain, a has the value 0, 1, or 2, b has the value 1, 2, or 3, c has the value 1 or 2, the sum of a + b + c = 4.

5. A method according to Claim 4 wherein the lactone is gamma butyrolactone or epsilon caprolactone.

6. A method according to either one of Claims 4 and 5 wherein R^4 represents a hydrogen atom and R″represents $(CH_2)_3$, $(CH_2)_3NHCH_2CH_2$, $CH_2CH(CH_3)CH_2NHCH_2CH_2$ or $(CH_2)_3NHCH_2CH_2NHCH_2CH_2$.

7. A method according to any one of Claims 4, 5 and 6 wherein the silane produced is hydrolysed to provide a polysiloxane.

8. A method according to any one of Claims 4, 5 and 6 wherein the silane produced is condensed to provide a polysiloxane.

9. A method according to Claim 4 substantially as hereinbefore described with reference to any one of Example silanes 1, 2 and 3.

10. An organosilane compound prepared by a method according to Claim 4.

11. An organosilane compound according to Claim 1 substantially as hereinbefore described especially with respect to Example silanes 1, 2 and 3.

DATED this 4th day of March, 1992

DOW CORNING LIMITED

WATERMARK PATENT AND TRADEMARK ATTORNEYS
THE ATRIUM
290 BURWOOD ROAD
HAWTHORN VICTORIA 3122

ABSTRACT

N-CONTAINING ORGANOSILANE COMPOUNDS

The specification describes and claims certain organosilane compounds and the preparation thereof. The organosilane compounds comprise a silane according to the general formula $R^1_aA_bSi(R''\text{-}NR'\text{-}X)_c$. A represents a hydroxyl or a hydrolysable group, R^1 represents a monovalent hydrocarbon group having up to 8 carbon atoms, R′ represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an alkenyl group or an aryl group, or a group X, R″ represents a divalent hydrocarbon group which may have nitrogen, oxygen or sulphur present in the carbon chain, X represents a group $CO(CHR)_nOH$ in which R represents a hydrogen atom or an alkyl group, a has the value 0, 1, or 2, b has the value 1, 2, or 3, c has the value 1 or 2, the sum of a + b + c = 4 and n has a value in the range 2 to 7.