COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

WACKER-CHEMIE GMBH

We hereby apply for the grant of a Patent for an invention entitled:

PROCESS FOR THE PREPARATION OF DIOrganopolysiloxanes
CONTAINING AN Si-BONDED HYDROXYL GROUP IN EACH OF THE TERMINAL UNITS

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered

P37 42 068.2

for a patent or similar protection made in Federal Republic of Germany on 11th December 1987

Our address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys, 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 8th day of December 1988

WACKER-CHEMIE GMBH

by

Ian A. Scott
Registered Patent Attorney

To:

THE COMMISSIONER OF PATENTS.
DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

In support of the Convention Application made by

WACKER-CHEMIE GmbH

(hereinafter referred to as the applicant) for a Patent

for an invention entitled:

PROCESS FOR THE PREPARATION

OF DIOGANOPOLYSILOXANES CONTAINING AN SI-BONDED HYDROXYL GROUP IN EACH OF THE TERMINAL UNITS.

I, Dr. Hans Stach and Dr. Erich Franke

Prinzregentenstrasse 22

8000 München 22, F R G

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 FEDERAL REPUBLIC OF GERMANY on the 11th day of DECEMBER, 1987, by

WACKER-CHEMIE GmbH

3. DR. KARL-HEINRICH WEGERHAUPT, of Marktler Strasse

78 D-8263 Burghausen, Germany; KARL BRAUNSPERGER, Unterhadermark 86, D-8263 Burghausen, Germany; DR. GUNTER VON AU, Lortzingweg 98, D-8263 Burghausen, Germany, and DR. FRIDOLIN STARY, of Gluckstrasse 9, D-8263, Burghausen, Germany, are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant would, if a patent were granted on an application made by the actual inventors, be entitled to have the patent assigned to it.

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 Munich this 13th day of October, 1988.

To: THE COMMISSIONER OF PATENTS.

Dr. Hans Stach
Director

Dr. Erich Franke
Head of Patent Licensing and Trademark Dept.
1. Process for the preparation of diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units, characterized in that a cyclic diorgano-polysiloxane and/or diorganodichlorosilane hydrolysis product is reacted with 0.1 to 3% by weight of diorganodichlorosilane, based on the weight of the particular amount of cyclic diorganopolysiloxane and/or diorganodichlorosilane hydrolysis product employed, in the presence of 1 to 50 ppm by weight of phosphonitrile chloride, based on the total weight of the particular amount of organo-silicon compounds employed, to give a diorganopolysiloxane containing an Si-bonded chlorine atom in each of the terminal units, the reaction mixture is then treated with water or an aqueous solution and, after the aqueous phase has been separated off, the low more boiling (sic) constituents are removed from the diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units by distillation.
Complete Specification for the invention entitled:

PROCESS FOR THE PREPARATION OF DIORGANOPOLYSILOXANES CONTAINING AN SI-BONDED HYDROXYL GROUP IN EACH OF THE TERMINAL UNITS

The following statement is a full description of this invention, including the best method of performing it known to us:
Process for the preparation of diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units

The invention relates to a process for the preparation of diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units.

It is known from British Patent Specification 1,195,761 (published on 24th June 1970, Wacker-Chemie GmbH) that organohalogenosilicon compounds can be prepared by reacting halogenosilicon compounds with organosiloxanes containing no Si-bonded halogen in the presence of phosphonitrile chloride.

The object was to provide a process for the preparation of diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units, in which the viscosity of these diorganopolysiloxanes can be purposefully controlled. There was furthermore the object of providing diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units from relatively readily accessible organosilicon compounds, with relatively little expenditure, in good yields and with a narrow molecular weight distribution. These objects are achieved by the invention.

The invention relates to a process for the preparation of diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units, characterized in that a cyclic diorganopolysiloxane and/or diorganodichlorosilane hydrolysis product is reacted with 0.1 to 3% by weight of diorganodichlorosilane, based on the weight of the particular amount of cyclic diorganopolysiloxane and/or diorganodichlorosilane hydrolysis product employed, in the presence of 1 to 50 ppm by weight of phosphonitrile chloride, based on the total weight of the
particular amount of organosilicon compounds employed, to give a diorganopolysiloxane containing an Si-bonded chlorine atom in each of the terminal units, the reaction mixture is then treated with water or an aqueous solution and, after the aqueous phase has been separated off, the low more boiling (sic) constituents are removed from the diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units by distillation.

According to British Patent Specification 1,195,761, very much larger amounts of halogenosilicon compounds and also of phosphonitrile chloride were used than in the process according to the invention. Moreover, nothing about the preparation of diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units or about a process for controlling the viscosity of these diorganopolysiloxanes was to be found from British Patent Specification 1,195,761, and this preparation and process also were not obvious.

The cyclic diorganopolysiloxane used in the process according to the invention is preferably one of the formula

\[(R_2SiO)_n\]

wherein \(R\) denotes identical or different, optionally halogenated hydrocarbon radicals having 1 to 18 carbon atom(s) per radical and \(n\) is an integer with a value of from 3 to 11.

One type of cyclic diorganopolysiloxane can be used. However, it is also possible to use a mixture of at least two different types of cyclic diorganopolysiloxanes, it being possible for the difference to result from different ring sizes and/or different substituents on the silicon atoms.

The diorganodichlorosilane hydrolysis product used in the process according to the invention is preferably one which consists of 20 to 30\% by weight of cyclic diorganopolysiloxane of the formula
and of 70 to 80% by weight of diorganopolysiloxane of the formula

\[ (R_2SiO)_n \]

in each case based on the weight of the particular amount of diorganodichlorosilane hydrolysis product employed, \( R \) and \( n \) having the meaning given for these symbols above and \( m \) being an integer with a value from 20 to 50.

The diorganodichlorosilane used in the process according to the invention is preferably one of the formula

\[ R_2SiCl_2 \]

wherein \( R \) has the meaning given above for this radical.

Examples of hydrocarbon radicals \( R \) are alkyl radical (sic), such as the methyl and ethyl radical and butyl, decyl and octadecyl radicals; hydrocarbon radicals with at least one aliphatic multiple bond, such as the vinyl radical; aryl radicals, such as the phenyl radical; alkaryl radicals, such as tolyl radicals; and aralkyl radicals, such as the benzyl radical. Examples of halogenated hydrocarbon radicals \( R \) are halogenoalkyl radicals, such as the 3,3,3-trifluoropropyl radical, and halogenoaryl radicals, such as o-, p- and m-chlorophenyl radicals. At least 70% of the number of organic radicals in the organosilicon compounds used in the process according to the invention are preferably methyl radicals, just because of easier accessibility.

The viscosity of the end product — the diorganopolysiloxane containing an Si-bonded hydroxyl group in each of the terminal units — can be purposefully controlled by the amount of diorganodichlorosilane, which is in the range from 0.1 to 3% by weight, in each case based on the weight of the particular amount of cyclic diorganopolysiloxane and/or diorganodichlorosilane hydrolysis product employed, with which the cyclic diorganopolysiloxane and/or
diorganodichlorosilane hydrolysis product is reacted.

The phosphonitrile chlorides in the presence of which the cyclic diorganopolysiloxane and/or diorganodichlorosilane hydrolysis product is reacted with the diorganodichlorosilane can be, for example, those which have been prepared by reaction of 400 parts by weight of phosphorus pentachloride with 130 parts by weight of ammonium chloride (compare, for example, "Bericht der Deutschen Chemischen Gesellschaft" ("Report of the German Chemical Society"), year 57, 1924, page 1345), or those which are obtained by reacting 2 mol of phosphorus pentachloride with 1 mol of ammonium chloride (compare, for example, U.S. Patent Specification 3,839,388, published on 1st October 1974, S. Nitzsche et al., Wacker-Chemie GmbH). Mixtures of at least two different types of phosphonitrile chlorides can of course also be used.

Phosphonitrile chloride is used in amounts of 1 to 50 ppm by weight, particularly preferably in amounts of 20 to 40 ppm by weight, in each case based on the weight of the particular amount of organosilicon compounds employed.

The reaction of the cyclic diorganopolysiloxane and/or diorganodichlorosilane hydrolysis product with the diorganodichlorosilane in the presence of phosphonitrile chloride is carried out at a temperature of preferably 60 to 100°C, particularly preferably 70 to 90°C, and preferably under the pressure of the surrounding atmosphere, that is to say at 1020 hPa (absolute) or about 1020 hPa (absolute). If desired, however, it is also possible to use higher or lower pressures during the reaction. The preferred reaction times are in the range from 3 to 8 hours.

After the reaction of the cyclic diorganopolysiloxane and/or diorganodichlorosilane hydrolysis product with the diorganodichlorosilane in the presence of phosphonitrile chloride to give the diorganopolysiloxane containing an Si-bonded chlorine atom in each of the terminal units, the reaction mixture is treated with water or an aqueous solution and the aqueous phase is then separated
off from the organic phase.

The reaction mixture is at the same time washed several times with liquid water in order to reduce the acid content of the reaction mixture. During the washing operation, both the phosphonitrile chloride and its reaction products are at the same time removed from the reaction mixture.

Instead of water as a liquid, it is also possible to use an alkali aqueous solution, for example an aqueous solution of NaHCO₃, in order to reduce the number of washing operations to one if appropriate.

The reaction mixture can also be treated with water in vapour form instead of with water in liquid form, in which case water in vapour form is passed through the reaction mixture. The treatment with steam has the advantage that the aqueous phase is separated off from the organic phase by passing steam through the reaction mixture and at the same time volatile constituents, such as, for example, unreacted cyclic diorganopolysiloxanes, are simultaneously driven off.

The reaction mixture is treated with water in liquid or vapour form or an aqueous solution until it has, preferably, a pH in the range from 5 to 9, particularly preferably of approximately 7.

If appropriate, for better separation of the organic phase from the aqueous phase, a water-immiscible inert organic solvent with a density of less than 1 g/cm³ at 20°C is added to the reaction mixture. Examples of suitable solvents are, for example, benzene, toluene or xylene. The solvents are added in amounts of up to 100% by weight, based on the weight of the particular amount of organosilicon compounds employed.

After the aqueous phase has been separated from the organic phase, any organic solvent added is removed from the organic phase by distillation.

The low more boiling (sic) constituents, which are, in particular, cyclic diorganopolysiloxanes, are separated off from the required diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units by
distillation. The distillation is preferably carried out at 140 to 150°C and under 0.5 to 8 hPa (absolute).

The diorganopolysiloxanes which are prepared by the process according to the invention and contain an Si-bonded hydroxyl group in each of the terminal units have a viscosity of preferably 250 to 50,000 mPa.s at 25°C and preferably contain 0.038 to 0.38% by weight of Si-bonded hydroxyl groups, in each case based on the weight of these diorganopolysiloxanes.

The diorganopolysiloxanes which are prepared by the process according to the invention and contain an Si-bonded hydroxyl group in each of the terminal units are excellently suitable for further condensation to give diorganopolysiloxanes of higher molecular weight. In particular, considerably less phosphonitrile chloride than previously is required for the further condensation in the presence of phosphonitrile chloride.

The diorganopolysiloxanes which are prepared according to the invention and contain an Si-bonded hydroxyl group in each of the terminal units are suitable, for example, as additives for compositions which are based on diorganopolysiloxanes and can be crosslinked at room temperature or higher temperatures.

The phosphonitrile chloride used in the following Examples was prepared as follows:

A mixture of 417 g (2 mol) of phosphorus pentachloride and 53.3 g (1 mol) of ammonium chloride in 1000 ml of tetrachloroethane is heated under reflux at the boiling point for 12 hours. The volatile constituents are removed from the resulting pale yellow solution at 160°C while reducing the pressure to about 1.33 hPa (sic) (absolute). Yellowish crystals which essentially consist of the compound of the formula

\[ \text{Cl}_3\text{PNPCl}_2\text{NPCl}_3 \cdot \text{PCl}_6 \]

remain as the residue.

**Example 1**

200 g of a mixture of cyclic dimethylpolysiloxanes
having 3 to 11 siloxane units per molecule, the content of octamethylcyclotetrasiloxane dominating the content of the other cyclic dimethylpolysiloxanes, are mixed with 2 g of dimethyldichlorosilane and 0.04 ml of a 25 percent strength by weight solution of phosphonitrile chloride in methylene chloride in a glass flask which can be heated and has a discharge tap, stirrer and distillation attachment. The reaction mixture is heated to 80°C and stirred slowly at 80°C for 5 hours. 100 ml of toluene are then added to the reaction mixture and the organic phase is washed several times with 200 ml of water each time until free from acid and until the organic phase has a pH of about 7. After the aqueous phase has been separated off, the toluene is removed from the organic phase by distillation. After the substances which boil at 140 to 150°C under 1 to 3 hPa (absolute) have been distilled off, 180 g (90% of theory) of a water-clear dimethylpolysiloxane containing an Si-bonded hydroxyl group in each of the terminal units and having a viscosity of 2,120 mPa.s at 25°C and a content of Si-bonded hydroxyl groups of 0.1% by weight are obtained.

Example 2 to 4

The procedure described in Example 1 is repeated with the modification that instead of the 2 g of dimethyldichlorosilane, in each case the amount of dimethyldichlorosilane stated in Table 1 is used. The particular yields of dimethylpolysiloxane containing an Si-bonded hydroxyl group in each of the terminal units, its particular viscosity and its particular content of Si-bonded hydroxyl groups are shown in Table 1. As can be seen from Table 1, the viscosity of the end product can be controlled by the amount of dimethyldichlorosilane employed.

Table 1:

<table>
<thead>
<tr>
<th>Examples</th>
<th>(CH₃)₂SiCl₂ Yield of di-</th>
<th>Viscosity OH content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g % by g % of theory</td>
<td>mPa.s (25°C) % by weight</td>
</tr>
<tr>
<td>1</td>
<td>2 1 180 90</td>
<td>2,120 0.1</td>
</tr>
<tr>
<td>2</td>
<td>4 2 170 85</td>
<td>500 0.19</td>
</tr>
</tbody>
</table>
Examples 5 to 9

The procedure in Example 1 is repeated in each case, with the modifications that instead of the 200 g of the mixture of cyclic dimethylpolysiloxanes used in that Example, 200 g of dimethyldichlorosilane hydrolysis product which consists to the extent of 30% by weight of a mixture of cyclic dimethylpolysiloxanes having 3 to 11 siloxane units per molecule and to the extent of 70% by weight of a mixture of dimethyldichlorosilane diols having 20 to 50 siloxane units per molecule are used, and instead of the 2 g of dimethyldichlorosilane in each case the amount of dimethyldichlorosilane stated in Table 2 is used. The particular yields of dimethylpolysiloxane containing an Si-bonded hydroxyl group in each of the terminal ... (sic), its particular viscosity and its particular content of Si-bonded hydroxyl groups are stated in Table 2. As can be seen from Table 2, the viscosity of the end product can be controlled by the amount of

Table 2:

<table>
<thead>
<tr>
<th>Examples</th>
<th>Yield of dimethylpolysiloxane</th>
<th>Viscosity mPa.s (25°C)</th>
<th>OH content % by weight</th>
<th>CH₃₂SiCl₂ g</th>
<th>CH₃₂SiCl₂ g % by weight 1)</th>
<th>Yield of dimethylpolysiloxane 2)</th>
<th>Viscosity mPa.s (25°C)</th>
<th>OH content % by weight 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>6</td>
<td>3</td>
<td>187</td>
<td>93.5</td>
<td>587</td>
<td>0.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>2</td>
<td>182</td>
<td>91</td>
<td>1,530</td>
<td>0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>1</td>
<td>177</td>
<td>88.5</td>
<td>3,130</td>
<td>0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.5</td>
<td>0.75</td>
<td>176</td>
<td>88</td>
<td>6,400</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0.5</td>
<td>174</td>
<td>87</td>
<td>24,000</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) Content of Si-bonded hydroxyl groups determined by the Zerewitenoff method
2) Based on the weight of dimethyldichlorosilane hydrolysis product employed
Example 10

The procedure of Example 1 is repeated with the modifications that no toluene is added to the reaction mixture after a reaction time of 5 hours and that instead of washing the organic phase with water in liquid form, steam is passed through the reaction mixture until the reaction mixture has a pH of about 7. The volatile constituents are simultaneously driven off, since on subsequent heating of the reaction mixture at 150°C and 1 hPa (absolute), nothing further is distilled off. 174 g (86% of theory) of a water-clear dimethylpolysiloxane containing an Si-bonded hydroxyl group in each of the terminal units and having a viscosity of 3,500 mPa.s at 25°C and a content of Si-bonded hydroxyl groups of 0.07% by weight remain as the residue.

The dimethylpolysiloxanes which are prepared in Examples 1 to 10 and contain an Si-bonded hydroxyl group in each of the terminal units have a narrow molecular weight distribution, determined by gel chromatography.

Example 11

This Example is intended to demonstrate that satisfactory yields of end product are already obtained after reaction times of 3 hours. For this, analogously to Example 1, 200 g of the mixture of cyclic diorgano-polysiloxanes having 3 to 11 siloxane units per molecule used in that example are mixed with 2 g of dimethyldichlorosilane and 0.04 ml of a 25 percent strength by weight solution of phosphonitrile chloride in methylene chloride. The reaction mixture is heated to 80°C and is stirred slowly at this temperature. During the reaction time, a 10 g sample is taken every hour. The samples are each heated in an open crucible at 220°C for 4 hours in order to remove the volatile constituents. The residues of the samples are shown in Table 3.
Table 3:

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>Residue of the 10 g sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour</td>
<td>4.97 g</td>
</tr>
<tr>
<td>2 hours</td>
<td>5.80 g</td>
</tr>
<tr>
<td>3 hours</td>
<td>7.88 g</td>
</tr>
<tr>
<td>4 hours</td>
<td>8.35 g</td>
</tr>
<tr>
<td>5 hours</td>
<td>8.58 g</td>
</tr>
<tr>
<td>8 hours</td>
<td>8.78 g</td>
</tr>
</tbody>
</table>

A yield of about 79% of theory of end product is obtained even after a reaction time of only 3 hours.
CLAIMS
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for the preparation of diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units, characterized in that a cyclic diorganopolysiloxane and/or diorganodichlorosilane hydrolysis product is reacted with 0.1 to 3% by weight of diorganodichlorosilane, based on the weight of the particular amount of cyclic diorganopolysiloxane and/or diorganodichlorosilane hydrolysis product employed, in the presence of 1 to 50 ppm by weight of phosphonitrile chloride, based on the total weight of the particular amount of organosilicon compounds employed, to give a diorganopolysiloxane containing an Si-bonded chlorine atom in each of the terminal units, the reaction mixture is then treated with water or an aqueous solution and, after the aqueous phase has been separated off, the low more boiling (sic) constituents are removed from the diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units by distillation.

2. Process according to Claim 1, characterized in that the cyclic diorganopolysiloxane used is one of the formula

\[(R_2SiO)_n\]

wherein \( R \) denotes identical or different, optionally halogenated hydrocarbon radicals having 1 to 18 carbon atoms per radical and \( n \) is an integer with a value of from 3 to 11.

3. Process according to Claim 1, characterized in that the diorganodichlorosilane hydrolysis product used is one which consists of 20 to 30% by weight of cyclic diorganopolysiloxane of the formula

\[(R_2SiO)_n\]

and of 70 to 80% by weight of diorganopolysiloxane of the formula
in each case based on the weight of the particular amount of diorganodichlorosilane hydrolysis product employed, R and n having the meaning given in Claim 2 and m being an integer with a value from 20 to 50.

4. Process according to Claim 1, characterized in that the diorganodichlorosilane used is one of the formula

\[ \text{HO}(\text{R}_2\text{SiO})_m\text{SiR}_2\text{OH} \]


5. Process according to Claim 1, 2 or 3, characterized in that the diorganopolysiloxanes containing an Si-bonded hydroxyl group in each of the terminal units are freed from constituents which boil at 140 to 150°C under 0.5 to 8 hPa (absolute).

6. A Diorganopolysiloxane whenever prepared by the process as claimed in any one of claims 1 to 5.

DATED this 8th day of December 1988.

WACKER-CHEMIE GMBH