TO: KSI/Scientific & Technical Information Division
Attention: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code KSI, the attached NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. : 3,763,204

Government or Corporate Employee : Government

Supplementary Corporate Source (if applicable) :

NASA Patent Case No. : MFS-20979-2

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of column No. 1 of the Specification, following the words "... with respect to an invention of ... ."

Elizabeth A. Carter
Enclosure
Copy of Patent cited above
Polymerizable Disilanols Having In-Chain Perfluoroalkyl Groups

William J. Patterson, Madison, and Donald E. Morris, Huntsville, Ala., assignors to the United States of America as represented by the Administrator of the National Aeronautics and Space Administration


Int. Cl. C07F 7/08

U.S. Cl. 260—448.2 D

4 Claims

Abstract of the Disclosure

Disilanols having the formula

\[ \text{R} \quad \text{HO—\( \text{Ar—(CF}_3\)\_x—\text{Ar}\—\text{Si—OH} \quad \text{R} \]}

where \( \text{R} \) is a monovalent hydrocarbon radical, \( \text{Ar} \) is an arylene group and \( \text{x} \) is from 2 to 8. The disilanols, when reacted with a diaminosilane and cured, produce polymeric material resistant to hydrocarbon fuels and stable at elevated temperatures.

Origin of the Invention

The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

Cross Reference to Related Applications

The invention described herein is a division of application Ser. No. 100,774, filed Dec. 22, 1970, now U.S. Patent No. 3,666,718.

Background of the Invention

This invention relates to fluorine-containing organosilicon compounds and more particularly to disilanols having in-chain perfluoroalkyl groups.

The successful development of hypersonic aircraft and certain types of reusable space shuttle vehicles will require the availability of improved high-temperature sealant materials. Fuel-tank sealants for such applications are resistant to hydrocarbon fuels and are stable under thermo-oxidative environments at elevated temperatures such as 450° F to 500° F. for extended periods. In addition, candidate sealant materials must be resistant to hydrocarbon fuels and stable under thermo-oxidative environments at elevated temperatures. Also, materials which show better thermal stability and materials which lack the required fuel resistance. Fuel resistance consistent with some improvement in thermal stability has been obtained in newly developed polymer systems which incorporate fluorine atoms along the polymer backbone or in pendant groups. However, most of the previous fluorine-containing sealant polymers have been deficient in their tendency to promote stress corrosion of titanium alloys, probably because of elimination of hydrogen and fluorine from adjacent carbon atoms in the form of HF, and in their marginal thermal stability. Polymerizable fluorine-containing compounds, tailored to provide fuel resistance and thermal stability without having a structure likely to release HF, are accordingly needed.

Summary of the Invention

The present invention is directed to disilanols having the formula

\[ \text{R} \quad \text{HO—\( \text{Ar—(CF}_3\)\_x—\text{Ar—Si—OH} \quad \text{R} \]}

where \( \text{R} \) is a monovalent hydrocarbon radical, \( \text{Ar} \) is an aryleneco group and \( \text{x} \) is from 2 to 8 and to a process for preparing the same by hydrolysis of the corresponding dihydride compound, which in turn is prepared by reaction of a dibromoaryl perfluoroalkane with a monochloro silane. Disilanols of the formula given above are useful for preparation of polymers by reaction with diaminosilanes. Upon curing with ethyl silicate the polymers are converted to elastomeric material showing superior resistance to hydrocarbon fuels, favorable thermal stability and a minimum tendency to promote corrosion of titanium alloys. This combination of properties is believed to result from incorporation of perfluoroalkyl groups between aryleneco groups in the polymer backbone by means of the novel disilanols.

It is therefore an object of this invention to provide polymerizable disilanols containing in-chain perfluoroalkyl groups and aromatic groups.

Another object is to provide a process for preparing such disilanols.

Still another object is to provide polymerizable sealant material that is resistant to hydrocarbon fuels and is stable at elevated temperatures.

Other objects and advantages of the invention will be apparent from the following detailed description and the appended claims.

Description of the Preferred Embodiment

Disilanols embodying the present invention are represented by the formula

\[ \text{R} \quad \text{HO—\( \text{Ar—(CF}_3\)\_x—\text{Ar—Si—OH} \quad \text{R} \]}

where \( \text{R} \) is a monovalent hydrocarbon radical, \( \text{Ar} \) is an aryleneco group and \( \text{x} \) is a whole number from 2 to 8. The monovalent hydrocarbon radical designated by \( \text{R} \) can be an alkyl radical such as methyl, ethyl, propyl, butyl and the like; an aryl radical such as phenyl, xylil, tolyl, etc.; an aralkyl radical such as phenylethyl or benzyl, a cycloaliphatic radical such as cyclohexyl, or any other monovalent aliphatic or aliphatic radical. The simpler disilanols having methyl or phenyl groups at these sites are preferred for use in polymer preparations. The aryleneco group designated by \( \text{Ar} \) can be any divalent aromatic group exemplified by p-phenylene, m-phenylene, biphenylene, naphthalene, phenylene ether, diphenylethylene and diphenylproplylene.

Disilanols having the formula given above can be prepared by hydrolysis of the corresponding dihydride com-
Polymerization proceeds readily upon heating an equimolar mixture of these reactants in a dry solvent such as toluene to a temperature of 90 to 100° C. The resulting polymer is a viscous oil having a degree of polymerization up to about 100, which polymer can be cured to form a tough, flexible thermoset elastomer. Curing can be carried out at room temperature by addition of an ethyl silicate cross-linking agent and a metal salt catalyst such as dibutyltin dilaurate at proportions of 10 and 2 weight percent, respectively. Other curing agents and catalysts can also be used. The invention is further illustrated by the following specific example.

Example 1

The following procedure exemplifies the preparation of a disilanol wherein R in the formula given above is methyl, Ar is 1,4-phenylene and x is 3. Perfluoro-glutaral chloride (200.0 grams, 0.722 mole) was treated with potassium iodide (320.0 grams, 1.93 moles) in a stirred pressure vessel for six hours at 200° C and 500-600 p.s.i. The product 1,3-didio-1,1,2,2,3,3-hexafluoropropionate, b. 105° C./350 mm., was obtained in 45 percent yield. The dido compound (140.0 grams, 0.347 mole) was then reacted with p-iodobromobenzene (216.0 grams, 0.763 mole) in the presence of 198 grams of an activated copper-bronze catalyst as dibutyltin dilaurate at proportions of 10 and 2 weight percent respectively. The resulting diol was then reacted with one mole of the diodo compound in an aprotic solvent such as N,N-dimethylformamide in the presence of an activated copper-bronze catalyst

The disilanol was then reacted with an equimolar amount of bis(dimethylamino)dimethylsilane by heating to a temperature of 90-100° C in dry toluene to form a viscous polymer having an inherent viscosity of 0.5 at a concentration of 1 gm./dl. in tetrahydrofuran at 30° C. A sample of the polymer was cured by addition of ethyl silicate and dibutyltin dilaurate at proportions of 10 and 2 weight percent respectively to produce tough, flexible thermoset elastomeric material. The elastomeric material showed no degradation, color change or loss of mechanical properties upon being boiled in water for 24 hours. The sample for 24 hours in JP-4 aviation fuel resulted in swelling of 30% of its original volume, as compared to 150% for conventional silicones.
What is claimed is:

1. A compound having the formula
\[
\text{R} \quad \text{R} \\
\text{HO-SI-}\text{Ar-}\{\text{CF}_x\}_x-\text{Si-}
\text{R} \quad \text{R} \\
\text{OH}
\]
where R is a monovalent hydrocarbon radical selected from the group consisting of methyl, ethyl and phenyl, Ar is a phenylene group and x is a whole number from 2 to 8.

2. The compound of claim 1 wherein R is a methyl radical.

3. The compound of claim 2 wherein Ar is p-phenylene.

4. The compound of claim 3 wherein x is 3.

References Cited

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Date</th>
<th>Inventor(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,561,429</td>
<td>7/1951</td>
<td>Sveda</td>
</tr>
<tr>
<td>3,647,740</td>
<td>3/1972</td>
<td>Loree et al.</td>
</tr>
<tr>
<td>3,666,718</td>
<td>5/1972</td>
<td>Patterson et al.</td>
</tr>
</tbody>
</table>

OTHER REFERENCES


10 DANIEL E. WYMAN, Primary Examiner
P. F. SHAVER, Assistant Examiner

U.S. Cl. X.R.

15 260—46.5 E, 448.2 E