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:

Yes [X] No [ ]

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
Disilanols having the formula
\[ \text{HO-Si-Ar-( CF}_{x}\text{)}_{m}-\text{Si-OR} \]
where \( R \) is a monovalent hydrocarbon radical, \( Ar \) is an arylene group and \( x \) 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 diamino- silanes. 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 arylene 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
\[ \text{HO-Si-Ar-( CF}_{x}\text{)}_{m}-\text{Si-OR} \]
where \( R \) is a monovalent hydrocarbon radical, \( Ar \) is an arylene group and \( x \) is a whole number from 2 to 8. The monovalent hydrocarbon radical designated by \( R \) can be an alkyl radical such as methyl, ethyl, propyl and the like; an aryl radical such as phenyl, xylyl, 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 prepared for use in polymer preparations. The arylene group designated by \( Ar \) can be any divalent aromatic group exemplified by p-phenylene, m-phenylene, biphenylene, naphthalene, phenylene ether, diphenylmethylene and diphenylpropylenes.

Disilanols having the formula given above can be prepared by hydrolysis of the corresponding dihydride com-
fuel resistance can be imparted into the polymer when R is a substituted pendant radical at these sites, additional carbon radical, defined herein to include fluorine-substituted radicals such as methyl radical, and R' is a monovalent hydrocarbon radical. Such a 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. Perflouoro-gluataryl chloride (200.0 grams, 0.722 mole) was treated with potassium iodide (320.0 grams, 1.95 moles) in a stirred pressure vessel for six hours at 200° C and 500–600 psig. The product, 1,3-diduro-1,1,2,2,3,3-hexafluoropropylene, b. 105° C./350 mm., was obtained in 45 percent yield. The disilanol (140.0 grams, 0.347 mole) was then reacted with p-chlorobromobenzene (216.0 grams, 0.763 mole) in the presence of 198 grams of an activated copper-bronze catalyst by slurrying in N,N-dimethylformamide (N,N-dimethylformamide). The product, 1,3-bis-(p-bromophenyl)-1,2,2,3,3-hexafluoropropylene was purified as a crystalline solid, m. 124–5° C. in 60 percent yield.

**Analysis—Calcd for C_{12}H_{28}BrF_{6} (percent): C, 38.99, H, 1.75, Br, 34.59. Found (percent): C, 38.2, H, 2.2, Br, 33.8.**

The resulting disilanol (130.0 grams, 0.282 mole) was slowly added as a solution in tetrahydrofuran to a mixture of magnesium turnings (15.0 grams, 0.564 mole) and dimethyl chlorosilane (53.3 grams, 0.564 mole) in 100 ml. of tetrahydrofuran, which was stirred and heated slightly. The product, 1,3-bis-(p-bromophenyl)-1,1,2,2,3,3-hexafluoropropylene was isolated by extraction with cyclohexane and recovered in 50% yield by distillation, b. 170° C./2.5 mm.**

**Analysis—Calcd for C_{12}H_{28}F_{14} (percent): C, 54.36, H, 5.28, Si 13.34. Found (percent): C, 53.7, H, 5.05, Si, 14.1.**

The resulting dihydride was hydrolyzed by treatment with an ethanol-sodium ethoxide solution, and a water-sodium hydroxide-methanol solution. The crude diol was precipitated in potassium hydrogen phosphate and recovered by extraction with carbon tetrachloride in 30% yield, m. 118° C., as 1,3-[p-(dimethylamino)phenyl]-1,1,2,2,3,3-hexafluoropropylene.

**Analysis—Calcd for C_{11}H_{28}F_{14}O_{2} (percent): C, 40.7, H, 16.4, O 8.2. Found (percent): C, 40.4, H, 16.4, O 8.3.**

The diol was then reacted with an equimolar amount of bis(dimethyamino)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. Soaking 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. It is to be understood that the above example is merely illustrative and that modifications and changes in the procedures and reaction conditions described therein can be employed without departing from the spirit and scope of the invention.
What is claimed is:
1. A compound having the formula
   \[ \text{R} \quad \text{R} \]
   \[ \text{HO-Si-} \quad \text{Ar-} \quad (\text{CF}_2)_x \quad \text{Si-} \quad \text{OH} \]
   \[ \text{R} \quad \text{R} \]
   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.