TO: KSI/Scientific & Technical Information Division
Attn: 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.: 3,801,617

Government or Corporate Employee: Hughes Aircraft Co.

Supplementary Corporate Source (if applicable): Los Angeles, CA

NASA Patent Case No.: MFS-32411-1

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 ..."

Bonnie L. Woerner
Enclosure
The present invention is directed to thiophenyl ether disiloxanes and trisiloxanes having the formula:

\[ \text{Si}(\text{OSi})_n\text{OR} \]

where X is an atom of hydrogen or halogen, n is an integer from 1 to 2, and R is an alkyl or aryl group which can be substituted. A preferred specific compound is 3-(phenylthio)phenyl-1,1,3,3,5,5-hexamethyltrisiloxane, which is obtained by adding thiophenyl chloride to a Grignard reagent of a bromine-substituted aryl radical and hydrolyzing the resulting compound with a trisiloxane compound. Compounds embodying the invention have favorable fluid properties at low temperatures and are resistant to radiation and to nuclear or solar radiation. They are useful as lubricants and as other functional fluids under severe conditions of temperature, radiation, and vacuum.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Thiophenyl ether disiloxanes and trisiloxanes embodying the invention are represented by the formula:

\[ \text{Si}(\text{OSi})_n\text{OR} \]

where X is an atom of hydrogen or halogen, n is an integer from 1 to 2, and R is an alkyl or aryl group which can be substituted.

**ORIGIN OF THE INVENTION**

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435, 42 U.S.C. 2457).

**ABSTRACT OF THE DISCLOSURE**

Thiophenyl ether siloxanes having the formula:

\[ \text{Si}(\text{OSi})_n\text{OR} \]

where X is a hydrogen or halogen atom or an alkyl, aryl or aralkyl radical, n and R are integers from 1 to 3, R is an integer from 1 to 2 and R is methyl or phenyl radicals. Compounds embodying the invention exhibit favorable properties for use as lubricants and functional fluids under severe conditions of temperature, radiation, and vacuum.

**SUMMARY OF THE INVENTION**

The present invention is directed to thiophenyl ether disiloxanes and trisiloxanes having low pour points and a high degree of radiation resistance, along with good lubricity and other properties favorable to their use as lubricant fluids or other functional fluids for service under extreme conditions. Substitution of sulfur for the phenyl group oxygen of ether siloxane compounds has been found in this invention to result in a marked improvement in lubricity, while the siloxane units provide substantially decreased pour points.

It is therefore an object of this invention to provide improved lubricant and functional fluids for service over a wide range of temperatures.

Another object is to provide lubricant fluids that are resistant to nuclear and solar radiation.

Still another object is to provide lubricant fluids having a low vapor pressure.

Yet another object is to provide aromatic-group-containing siloxane compounds having low pour points and good lubricity.

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

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Thiophenyl ether disiloxanes and trisiloxanes embodying the invention are represented by the formula:

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**BACKGROUND OF THE INVENTION**

This invention relates to organosilicon compounds and to lubricant fluids for service under extreme conditions. Presently available lubricant base fluids fail to meet all of the requirements imposed for use in advanced space propulsion systems, and particularly for applications involving exposure to nuclear or solar radiation. In addition to a high degree of radiation resistance, lubricant fluids for such applications should exhibit liquidity over a wide temperature range, such as —50° F. to +500° F., a vapor pressure low enough for use in the high vacuum of space and good lubricity. Polyphenyl ether compounds have been found to have good radiation resistance and lubricity, but no individual polyphenyl ether has the combined properties of fluidity at ambient and lower temperatures and low volatility in vacuum. Other chemical compounds which exhibit favorable fluid properties at low temperatures, for example, silicones, have poor resistance to radiation, poor lubricity or excess volatility in vacuum.

One approach to attainment of improved overall fluid properties has been to synthesize compounds containing both aromatic ether groups characteristic of radiation resistance and thermal stability and siloxane groups of low-temperature fluid silicones. Ether siloxane compounds of the type disclosed in U.S. Pat. No. 3,114,759 show good radiation resistance and effective fluid properties at moderate to high temperatures, but their pour points are too high for many applications, and their lubricity is relatively low.

**SUMMARY OF THE INVENTION**

The present invention is directed to thiophenyl ether disiloxanes and trisiloxanes having low pour points and a high degree of radiation resistance, along with good lubricity and other properties favorable to their use as lubricant fluids or other functional fluids for service under extreme conditions. Substitution of sulfur for the phenyl group oxygen of ether siloxane compounds has been found in this invention to result in a marked improvement in lubricity, while the siloxane units provide substantially decreased pour points.

It is therefore an object of this invention to provide improved lubricant and functional fluids for service over a wide range of temperatures.

Another object is to provide lubricant fluids that are resistant to nuclear and solar radiation.

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

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Thiophenyl ether disiloxanes and trisiloxanes embodying the invention are represented by the formula:

\[ \text{Si}(\text{OSi})_n\text{OR} \]

where X is an atom of hydrogen or halogen, n is an integer from 1 to 2, and R is an alkyl or aryl group which can be substituted.
1,3-bis(phenylthio)phenyl - 1,1,3,3 - tetramethylsiloxane was prepared by the following procedure. To a solution of 108 grams of sodium methoxide in 750 ml. of absolute ethanol was added 220 grams of benzethiol. After refluxing for four hours, the solvent was distilled under vacuum, leaving 261.5 grams of sodium thiophenoxide in the form of a white product. A solution of 132 grams of absolute ethanol was added 220 grams of benzenethiol in 200 ml. of bis(2-methoxyethyl) ether. The mixture was refluxed for six hours, the solvent was distilled, and the residue was filtered through a glass fiber filter. 

EXAMPLE 2

1,3-bis(4-chlorophenylthio)phenyl - 1,1,3,3 - tetramethylsiloxane was prepared by the following procedure. To a solution of 108 grams of sodium methoxide in 750 ml. of absolute ethanol was added 289.3 grams of 4-chlorothiophenoxide. After refluxing for 1.5 hours, excess water and dioxane were removed under vacuum. The residue was washed with methanol and then distilled in carbon tetrachloride. This solution was passed through a column of neutral alumina. The solvent was evaporated under vacuum, and the residue was filtered through a fiber glass filter. 28.7 grams of 1,3-bis(4-chlorophenylthio)phenyl - 1,1,3,3-tetramethylsiloxane product was recovered.
where X is a hydrogen atom, a halogen atom or an alkyl, aryl, alkaryl or aralkyl radical, \( n_1 \) and \( n_2 \) are integers from 1 to 3, inclusive, \( n_3 \) is an integer from 1 to 2, inclusive, and \( R_1 \) and \( R_2 \) are methyl or phenyl radicals.

2. Siloxane compounds of claim 1 wherein X is a hydrogen atom, a halogen atom or a hydrocarbon radical selected from the group consisting of methyl, ethyl, propyl, phenyl, biphenyl, naphthyl, tolyl, xylol, benzyl or phenylethyl radicals.

3. The compound of claim 2 wherein X is a hydrogen atom, \( n_1 \) and \( n_3 \) are 1, \( n_2 \) is 2 and \( R_1 \) and \( R_2 \) are methyl radicals.

4. The compound of claim 2 wherein X is a hydrogen atom, \( n_1 \) and \( n_3 \) are 1, \( n_2 \) is 1 and \( R_1 \) and \( R_2 \) are methyl radicals.

5. The compound of claim 2 wherein X is chlorine, \( n_1 \) and \( n_3 \) are 1, \( n_2 \) is 1 and \( R_1 \) and \( R_2 \) are methyl radicals.

References Cited

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U.S. Cl. X.R.

252—496; 78