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-22411-1

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

YES ☒ 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
THIOPHENYL ETHER DISILOXANES AND TRISILOXANES USEFUL AS LUBRICANT FLUIDS Patent (NASA-Case-MFS-22411-1) THIOPHENYL ETHER DISILOXANES AND TRISILOXANES USEFUL AS LUBRICANT FLUIDS

James C. Fletcher, Administrator of the National Aeronautics and Space Administration, with respect to an invention of Norman Bilow and Richard I. Akawie, Los Angeles, Calif.

No Drawing. Filed July 24, 1973, Ser. No. 382,262

Int. Cl. C081 7/08

U.S. Cl. 260—448.2 N

5 Claims

ABSTRACT OF THE DISCLOSURE

Thiophenyl ether siloxanes having the formula

\[ \text{X} - \text{Si} - (\text{CH}_3)_{3-n} \text{CH}_2 \text{O} - \text{Si} - (\text{CH}_3)_{3-n} \text{CH}_2 \text{X} \]

where \( X \) is a hydrogen or halogen atom or an alkyl, aryl or alkenyl radical, \( n_1 \) and \( n_2 \) are integers from 1 to 3, \( n_3 \) is an integer from 1 to 2 and \( R_1 \) and \( R_2 \) are 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.

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).

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 phenoxyl 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.

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.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

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

\[ \text{X} - \text{Si} - (\text{CH}_3)_{3-n} \text{CH}_2 \text{O} - \text{Si} - (\text{CH}_3)_{3-n} \text{CH}_2 \text{X} \]

where \( X \) is an atom of hydrogen or a halogen such as chlorine or bromine; an alkyl radical including methyl, ethyl, propyl and the like; an aryl radical such as phenyl, biphenyl, naphthyl, tolyl or xylyl; an alkenyl radical such as benzyl or phenylethyl or an alkaryl 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. The most preferred specific compound, owing to its low pour point (—5°F.), good radiation resistance and lubricity properties on a par with commercially available polyphenyl ether lubricants, is 1,5-bis [3-(phenylthio)phenyl] - 1,1,3,3,5,5-hexamethyltrisiloxane.

Chlorine-substituted compounds, exemplified by 1,3-bis[3-(4-chlorophenylthio)phenyl] - 1,1,3,3,5,5-hexamethyltrisiloxane, show outstanding lubricity, but a higher pour point (+5°F. for the named compound). Another specific compound embodying the invention is 1,3-bis [3-(phenylthio)phenyl]-1,1,3,3,5,5-hexamethyltrisiloxane.

Novel siloxane compounds of this invention can be prepared by procedures similar to those previously used for preparing ether siloxanes, with a sulfur-containing reactant being substituted for the corresponding oxygen-containing ether compound. Disiloxanes are preferably prepared by reacting the Grignard reagent of a bromine-substituted phenylhydrobenzene with a dichlorosilane and hydrolyzing the resulting arylthiophenylvlchlorosilane with water. Trisiloxanes can be prepared by reacting the above-mentioned Grignard reagent with a trisiloxane compound obtained by partial hydrolysis of the appropriate dichlorosilane such as dimethyl-dichlorosilane.

Compounds embodying the invention exhibit favorable overall properties for use as lubricant fluids in space of other severe environments. In addition to their good lubricity, resistance to radiation and liquidity over a wide temperature range, these compounds have a low vapor pressure, resistance to oxidation and thermal degradation at temperatures over 500°F. and good miscibility with lubricant additives. Other properties of the compounds, in particular, high bulk moduli and high surface tension, indicate their suitability for use as working fluids for use under severe conditions, for example, as hydraulic fluids in spacecraft hydraulic servomechanisms.

The invention is further illustrated by the following specific examples.
siloxane 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 benzethanol. 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 water in 200 ml. of bis(2-methoxyethyl) ether was added dropwise during two hours to a solution of 236 grams of d-mibromobenzene in 200 ml. of bis(2-methoxyethyl) ether. The mixture was refluxed 22 hours longer and poured into a large amount of water. The brown oil which separated was washed several times with water, decolorized with charcoal, dried over potassium carbonate and distilled. After unreacted d-mibromobenzene was collected, 121.5 grams of product 1-bromo-3-(phenylthio)benzene distilled at 157-160 °C. at 3 torr was recovered. A solution of 115 grams of the 1-bromo-3-(phenylthio)benzene in 100 ml. of tetrahydrofuran was added with stirring during three hours to 17 grams of magnesium suspended in tetrahydrofuran. Formation of the Grignard reagent was initiated with a small amount of 1-iodobutane. After stirring for 3 hours longer, the Grignard reagent was decanted and added slowly during 2 hours to 122 ml. of dimethylchlorosilane. After stirring overnight, the tetrahydrofuran and excess dimethylchlorosilane were distilled. Carbon tetrachloride was added, and the insoluble salt was separated by filtration. The filtrate was then heated up to 185 °C. at 3 torr to remove volatile components from the product. 13-(phenylthio)phenyl dimethyldichlorosilane was recovered at a yield of 73 percent of theoretical. A solution of 10 ml. of water in 30 ml. of dioxane was then added dropwise with stirring to a solution of 41.5 grams of the 13-(phenylthio)phenyl dimethyldichlorosilane in 70 ml. of dioxane. After refluxing for 1.5 hours, the excess water and dioxane were removed under vacuum. The residue was washed with water and with methanol and then was dissolved 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. 42.7 grams of 1,3-bis[3-(4-chlorophenylthio)phenyl]-1,3,3,5,5,5-hexamethyltrisiloxane was recovered.

**Example 3**

1.5-bis[3-(phenylthio)phenyl]-1,1,3,3,5,5-hexamethyltrisiloxane was prepared by the following procedure. A solution of 53 grams of water in 60 ml. of dioxane was added dropwise with stirring during two hours to a solution of 750 grams of dimethyldichlorosilane in 750 ml. of anhydrous ethyl ether. The solution was then distilled through a short Vigreux column to separate the solvents. The higher boiling material was then redistilled through a 16-inch Vigreux column. The fraction distilling at 136-140 °C. at 760 torr (1,3-dichloro-1,1,3,3-tetramethyldisiloxane) weighed 136.6 grams and the fraction distilling at 174-178 °C. at 760 torr (1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane) weighed 76.7 grams. A solution of 115.8 grams of 1-bromo-3-(phenylthio)benzene in 500 ml. of anhydrous tetrahydrofuran was added slowly to 10.6 grams of magnesium in tetrahydrofuran. For-
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, \( n_2 \) 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, xylyl, benzyl or phenylethyl radicals.

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

References Cited

UNITED STATES PATENTS

2,863,898 12/1958 Merker ............ 260—448.2 N
3,914,548 11/1959 Schroll ............ 260—448.2 N
2,967,192 1/1961 Kantor ............ 260—448.2 N
2,544,296 3/1951 Burkhard .......... 260—448.2 N

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