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O'Lenick, Jr.

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[54] **ALKYL FLUORINATED SILICONE
POLYMERS**

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[73] Assignee: **Siltech Inc.**, Norcross, Ga.

[21] Appl. No.: **430,857**

[22] Filed: **Apr. 28, 1995**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 356,551, Dec. 15, 1994,
Pat. No. 5,446,114.

[51] **Int. Cl.⁶** **C08G 77/08**

[52] **U.S. Cl.** **528/15; 528/25; 528/42;
528/31; 556/454; 556/479**

[58] **Field of Search** **528/15, 25, 42;
556/479, 454**

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,992,521 2/1991 Saho et al. .

5,047,492 9/1991 Saho et al. .

Primary Examiner—Melvyn I. Marquis

[57] **ABSTRACT**

The invention relates to a series of novel silicone polymers containing both fluorinated and alkyl side chains. This class of compounds provides very thin breathable barriers which are very durable when applied to textiles and paper. The compounds of the present invention are prepared by reacting a silanic hydrogen containing silicone polymer with a vinyl containing fluoro compound and an alpha olefin.

10 Claims, No Drawings

ALKYL FLUORINATED SILICONE POLYMERS

This application is a continuation in part of application Ser. No. 356,551 filed Dec. 15, 1994, U.S. Pat. No. 5,446, 114.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a series of novel silicone polymers containing both fluorine groups and alkyl groups. This class of compounds provides thin durable breathable barriers when applied to textiles and paper. The presence of (a) silicone backbone, (b) a fluorine containing pendant group and (c) a separate alkyl group containing is critical to the functionality of the molecule. If the fluorine containing group is lacking in the molecule, the desired impermeability and thin film formation is not achieved. If the alkyl group is lacking in the molecule, the barrier is lacks durability. Only when the correct combination of groups are placed in the molecule is the desired material achieved. By "oil" we mean water insoluble materials including triglycerides like soybean oil, refined oils like motor oil, and silicone oil.

The compounds of the present invention are prepared by reacting a silanic hydrogen containing silicone polymer with a vinyl containing fluoro compound and an alpha olefin.

The compounds find application in a variety of applications, most importantly the textile and paper. The thin durable barrier is of interest in a variety of textile applications.

2. Arts and Practices

Silicone compounds have been known to be active at the surface of cellulosic and synthetic fibers as well as paper. They are good nondurable lubricants and are very stable to oxidation, however, their high cost and lack of efficiency at low concentrations as well as low durability have made their acceptance in commercial products quite low.

In addition to their high cost, silicone compounds have little or no solubility in mineral oils, fatty triglycerides and other classical fatty quaternary compounds used for softening. This has resulted in the inability to prepare stable blends for use as a textile fiber treatment.

In many applications, there is a desire for a more fatty soluble softener. The desired molecule should have the desirable softening and antistatic properties of silicone, yet have compatibility with traditional fatty materials and oils. Even though a textile softener which has both the desirable softening and antistatic properties of silicone as well as compatibility with fatty compounds has been a long felt need, it isn't until the compounds of the present invention that such a system has been attained.

U.S. Pat. No. 3,511,699 to Steman issued May 12, 1970 teaches that epoxy compounds placed in the silicone backbone by hydrosilation can be cured onto certain fibers to give improved substantivity. The substantivity is based upon the reaction of hydroxyl groups on the cellulosic and the epoxy group in the silicone polymer.

U.S. Pat. No. 5,164,471 issued in October 1992 to O'Lenick teaches that fluoro polyesters of silanols can be prepared by the reaction of a silanol, fluorine containing alcohol and a diacid.

None of these cited patents teach the incorporation of alkyl group and a separate fluorine containing group on the silicone backbone necessary to achieve the desired proper-

ties of the compounds of the present invention.

THE INVENTION

Object of the Invention

It is the object of the present invention to provide novel silicone polymers which contain both alkyl groups and fluorine groups. This combination offers a combination of thin and durable barrier properties.

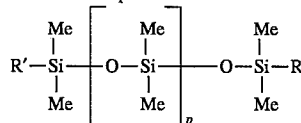
Summary of the Invention

The present invention relates to a series of novel silicone polymers which contain both fluorine and alkyl groups directly on silicone. The compounds of the present invention are prepared by reacting a silanic hydrogen containing silicone polymer with a vinyl containing fluoro compound and an alpha olefin.

As will become clear from the disclosure, the compounds of the present invention having silicone present in the molecule, fluorine present and a alkyl group present, all these result in the durable thin hydrophobic film.

The compounds of the present invention conform to the following structure;

Terminal Compounds



wherein;

p is an integer ranging from 1 to 2,000;

Me is methyl;

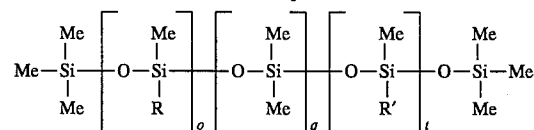
R' is $-(\text{CH}_2)_a-\text{CH}_3$

R is $-(\text{CH}_2)_2-(\text{CF}_2)_s-\text{CF}_3$;

s is an integer ranging from 1 to 13;

a is an integer ranging from 5 to 21.

Comb Compounds



wherein;

Me is methyl;

o is an integer ranging from 1 to 20;

t is an integer ranging from 1 to 20;

q is an integer ranging from 0 to 2000;

R' is $-(\text{CH}_2)_a-\text{CH}_3$

R is $-(\text{CH}_2)_2-(\text{CF}_2)_s-\text{CF}_3$;

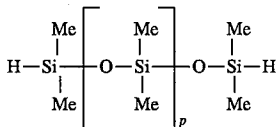
s is an integer ranging from 1 to 13;

a is an integer ranging from 5 to 21.

Silanic hydrogen containing compounds, used as raw materials in the preparation of the compounds of the present invention, are known to those skilled in the art. They conform to the following structures:

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Terminal Silanic Hydrogen Polymers

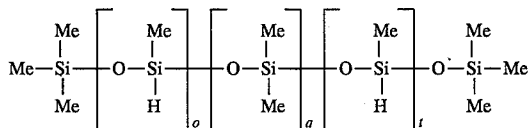


wherein;

Me is methyl;

p is an integer ranging from 1 to 2,000.

Comb Silanic Hydrogen Intermediates



wherein;

Me is methyl;

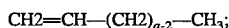
o is an integer ranging from 1 to 20;

t is an integer ranging from 1 to 20;

q is an integer ranging from 0 to 2000.

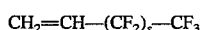
These materials are one of the basic raw materials used in the preparation of the compounds of the present invention.

The silanic hydrogen compounds are reacted with (a) alpha olefin alcohol conforming to the following structure;



a is an integer ranging from 5 to 21.

and (b) vinyl containing fluoro compounds conforming to the following structure:



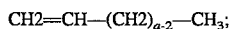
s is an integer ranging from 1 to 13.

EXAMPLES

Raw Materials

A) Alpha Olefin

Alpha olefins conform to the following structure and are commercially available from various sources. They conform to the following structure:



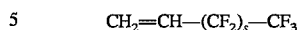
a is an integer ranging from 5 to 21.

Example	a
1	5
2	7
3	9
4	11
5	13
6	15
7	17
8	19
9	21

B) Fluoro Vinyl Intermediate

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Fluoro Vinyl intermediates are commercially available from a variety of sources including DuPont. They conform to the following structure:



s is an integer ranging from 1 to 13. These materials are available from Dupont.

Fluoro Vinyl Intermediates	
Example	s
10	1
11	5
12	7
13	11
14	13

C.) Silanic Hydrogen Containing Intermediates

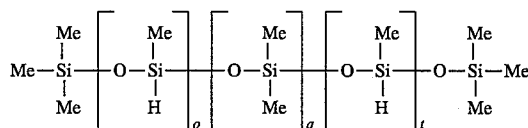
The preferred method of placing the alkyl or fluoro group is by the reaction of silanic hydrogen containing polymer with either the fluoro vinyl or alpha olefin. This technology is carried out using the same process as is well known to those skilled in the art and are described in U.S. Pat. No. 4,083,856.

Preparation of Silanic Hydrogen Containing Intermediates

Silicone intermediates of the type used to make the compounds of this invention are well known to those skilled in the art. U.S. Pat. No. 5,159,096 issued to Austin in November 1992, incorporated herein by reference discloses the basic chemistry of hydrosilation.

International Publication (Silicone Alkylene Oxide Copolymers As Foam Control Agents) WO 86/0541 by Paul Austin (Sep. 25, 1986) p.16 also teaches how to make these intermediates. The intermediates listed below are available from Siltech Inc. Norcross Ga. 30093 and are marketed under the Silseal tradename:

Silanic Hydrogen Containing Compounds(Comb Type)



wherein;

Me is methyl;

o is an integer ranging from 1 to 20;

t is an integer ranging from 1 to 20;

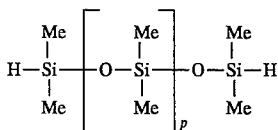
q is an integer ranging from 0 to 2000.

Example	o	t	q
15	1	1	1
16	10	20	50
17	20	10	2000

Silanic Hydrogen Containing Compounds

(Terminal Type)

-continued



wherein;

Me is methyl;

p is an integer ranging from 1 to 2,000.

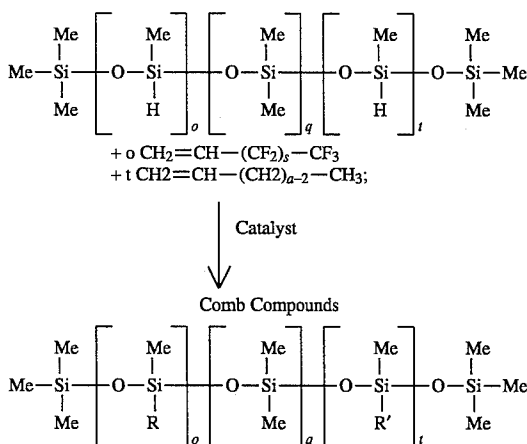
Silanic Hydrogen Containing Compounds

Example	p
18	2000
19	500
20	1

The intermediates listed below are available from Siltech Inc. Norcross Ga. 30093 and are marketed under the Silseal tradename:

Hydrosilation Reactions

The hydrosilation reaction is carried out according to the following reaction scheme:



wherein;

Me is methyl;

o is an integer ranging from 1 to 20;

t is an integer ranging from 1 to 20;

q is an integer ranging from 0 to 2000;

R' is $-(\text{CH}_2)_a-\text{CH}_3$ R is $-(\text{CH}_2)_2-(\text{CF}_2)_s-\text{CF}_3$;

s is an integer ranging from 1 to 13;

a is an integer ranging from 5 to 21.

Process

As stated previously, the hydrosilation process used to make the compounds of this invention are well known to those skilled in the art. One of many references is International Publication (Silicone Alkylene Oxide Copolymers As

Foam Control Agents) WO 86/0541 by Paul Austin (Sep. 25, 1986) p.19.

General Procedure

To a suitable flask fitted with a mechanical agitator, thermometer with a Therm-o-watch temperature regulator, nitrogen sparge tube vented reflux condenser and heating mantle is added the specified quantity of the specified Alpha Olefin Example 1-9, and the specified quantity of the specified Fluoro Vinyl Intermediate Example 10-14. Next is added the specified number of grams of the specified hydrosilation intermediate Example #15-20 and 3,000 grams of toluene. Heat to 115 C. to remove azeotropically remove any water and 200 ml of toluene. The temperature is reduced to 85 C. and 3.5 ml of 3% H₂PtCl₆ in ethanol is added. Light to then excluded from the flask by covering it with a black cloth. An exotherm is noted to about 95 C., while the contents are stirred for about 2 hours. During this time silanic hydrogen concentration drops to nil. Cool to 65 C. and slowly add 60 g of sodium bicarbonate. allow to mix overnight and filter through a 4 micron pad. Distill off any toluene at 100 C. and 1 torr.

Example 21

To a suitable flask fitted with a mechanical agitator, thermometer with a Therm-o-watch temperature regulator, nitrogen sparge tube vented reflux condenser and heating mantle is added 84.0 grams of Alpha Olefin Example 1, 108.0 grams of Fluoro Vinyl Intermediate Example 10, Next is added 358.0 grams of hydrosilation intermediate (Example # 15) and 3,000 grams of toluene. Heat to 115 C. to remove azeotropically remove any water and 200 ml of toluene. The temperature is reduced to 85 C. and 3.5 ml of 3% H₂ PtCl₆ in ethanol is added. Light to then excluded from the flask by covering it with a black cloth. An exotherm is noted to about 95 C., while the contents are stirred for about 2 hours. During this time silanic hydrogen concentration drops to nil. Cool to 65 C. and slowly add 60 g of sodium bicarbonate. allow to mix overnight and filter through a 4 micron pad. Distill off any toluene at 100 C. and 1 torr.

Examples 22-34

Example 21 is repeated, only this time replacing the alpha olefin intermediate with the specified number of grams of the specified alpha olefin, replacing the Fluoro Vinyl Intermediate with the specified number of grams of the specified Fluoro Vinyl Intermediate and replacing the specified hydrosilation intermediate with the specified type and number of grams of the specified hydrosilation intermediate.

Example Ex	Alpha Olefin Intermediate Ex Grams	Fluoro Vinyl Intermediate Ex Grams	Hydrosilation Intermediate Ex Grams
22	2 112.0	11 308.0	16 377.0
23	3 140.0	12 408.0	17 1000.0
24	4 168.0	13 558.0	18 148134.0
25	5 196.0	14 708.0	19 37143.0
26	6 224.0	10 108.0	20 208.0
27	7 252.0	11 308.0	15 358.0
28	8 280.0	12 408.0	16 377.0
29	9 308.0	13 558.0	17 1000.0
30	1 84.0	14 708.0	18 148134.0
31	2 112.0	10 108.0	19 37134.0
32	3 168.0	11 308.0	20 208.0

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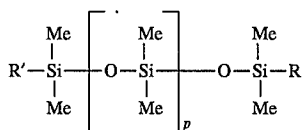
-continued

Example Ex	Alpha Olefin Intermediate Ex Grams	Fluoro Vinyl Intermediate Ex Grams	Hydrosilation Intermediate Ex Grams
33	4 196.0	12 408.0	15 358.0
34	5 224.0	13 558.0	16 377.0

It will be understood that the mole ratio of fluoro vinyl intermediate+the mole ratio of alpha olefin to the mole ratio of hydrosilation intermediate will range from 0.9 to 1.0 to 1.2 to 1.0 with a preferred ratio of 1.1 to 1.0. This will mean that under the preferred situation there will be a slight excess of fluoro vinyl intermediate+the mole ratio of alpha olefin relative to hydrosilation intermediate.

What is claimed:

1. A polymer which conforms to the following structure:



wherein;

p is an integer ranging from 1 to 2,000;

Me is methyl;

R' is $-(\text{CH}_2)_a-\text{CH}_3$;

R is $-(\text{CH}_2)_2-(\text{CF}_2)_s-\text{CF}_3$;

s is an integer ranging from 1 to 13;

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a is an integer ranging from 5 to 21.

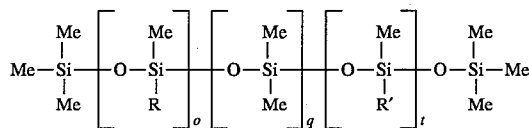
2. A compound of claim 1 wherein s is 13.

3. A compound of claim 1 wherein s is 5.

4. A compound of claim 1 wherein s is 7.

5. A compound of claim 1 wherein s is 11.

6. A polymer which conforms to the following structure:



wherein;

Me is methyl;

o is an integer ranging from 1 to 20;

t is an integer ranging from 1 to 20;

q is an integer ranging from 0 to 2000;

R' is $-(\text{CH}_2)_a-\text{CH}_3$;

R is $-(\text{CH}_2)_2-(\text{CF}_2)_s-\text{CF}_3$;

s is an integer ranging from 1 to 13;

a is an integer ranging from 5 to 21.

7. A compound of claim 6 wherein s is 13.

8. A compound of claim 6 wherein s is 5.

9. A compound of claim 6 wherein s is 7.

10. A compound of claim 6 wherein s is 11.

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