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Lee

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**[54] POLYIMIDESILOXANES AND METHODS FOR THEIR PREPARATION AND USE**[75] Inventor: **Chung J. Lee**, Amherst, N.Y.[73] Assignee: **Occidental Chemical Corporation**,  
Niagara Falls, N.Y.

[21] Appl. No.: 655,888

[22] Filed: **Feb. 15, 1991****Related U.S. Patent Documents**

Reissue of:

[64] Patent No.: **4,957,993**  
Issued: **Sep. 18, 1990**  
Appl. No.: **270,920**  
Filed: **Nov. 14, 1988**[51] Int. Cl.<sup>5</sup> ..... **B05D 3/02; C08F 2/46;**  
**C08G 77/04**[52] U.S. Cl. .... **528/26; 528/28;**  
**528/38**[58] Field of Search ..... **528/26, 28, 38****[56] References Cited****U.S. PATENT DOCUMENTS**

3,325,450	6/1967	Holub .	
3,424,718	1/1969	Angelo .	
3,553,282	5/1971	Holub .	
3,847,867	11/1974	Heath et al. .	
4,290,936	9/1981	Sasaki et al. .	
4,395,527	7/1983	Berger .	
4,404,350	9/1983	Ryang .	
4,480,009	10/1984	Berger .	
4,520,075	5/1985	Igarashi et al. .	
4,535,099	8/1985	Lee et al. .	
4,586,997	5/1986	Lee .	
4,588,804	5/1986	Fryd .	
4,612,361	9/1986	Peters .	
4,634,760	1/1987	Takekoshi et al. .	
4,645,824	2/1987	Landis et al. .	
4,670,497	6/1987	Lee .	
4,760,126	7/1988	Numata et al. .	
4,849,490	7/1989	Borthelmy	528/26
4,853,452	8/1989	Lee	528/26

**FOREIGN PATENT DOCUMENTS**7473 1/1983 Japan .  
13631 1/1983 Japan .**OTHER PUBLICATIONS**V. H. Kukertz, *Macromol. Chem.* 98, 1966 (pp. 101-108).McGrath et al, *Polymer Preprints*, 27 (2), 1986 (p. 403).  
*Chem. Abstracts* CA:62 14585b (1965), published Dec. 18, 1964.

Copen ding Appln. Ser. No. 154,168, filed Feb. 9, 1988.

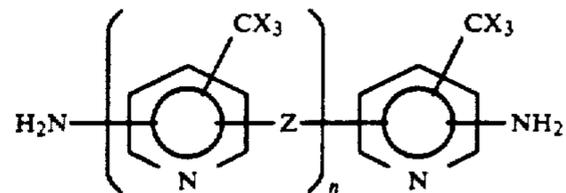
Copen ding Appln. Ser. No. 205,412, filed Jun. 10, 1988.

Copen ding Appln. Ser. No. 239,372, filed Sep. 1, 1988.

*Primary Examiner*—Morton Foelak*Attorney, Agent, or Firm*—James F. Tao; Richard D. Fuerle**[57] ABSTRACT**

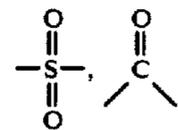
Substantially fully imidized polyimidesiloxanes which are based on a selected pyridine compound are soluble

in diglyme which gives them particular utility in the micro-electronics industry. The polymers are prepared from the dianhydride, a difunctional siloxane monomer and an organic diamine that has the formula

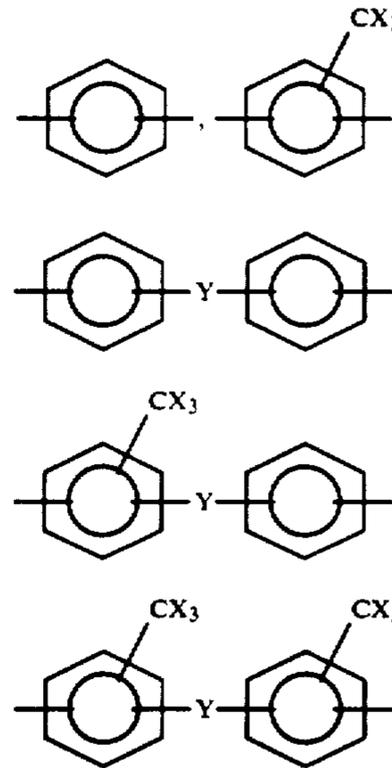


wherein X is hydrogen, halide, phenyl or combinations thereof,

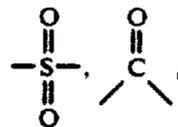
Z = —O—, —S—,

>C(CX<sub>3</sub>)<sub>2</sub>, —, or —Y—Ar—Y—.

Ar =



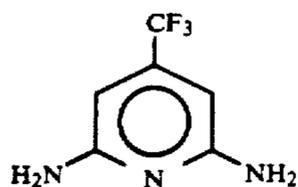
Y = —O—, —S—,

>C(CH<sub>3</sub>)<sub>2</sub>, or —.

n = 0 or 1.

The preferred diamine has the formula

(Abstract continued on next page.)



Other diamines can be used to provide an asymmetrical structure in the polyimidesiloxane polymer chain. The polyimidesiloxane can be prepared with functional groups which render them directly curable. The

polyimidesiloxanes can also be prepared with functional groups which when reacted with an unsaturated compound renders the polymers curable. The products of the invention can be used in the form of solutions in the micro-electronic industry. The polymers can also be used in wire and cable coating and to prepare films, fibers, and molded and extruded articles.

57 Claims, No Drawings

## POLYIMIDESILOXANES AND METHODS FOR THEIR PREPARATION AND USE

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

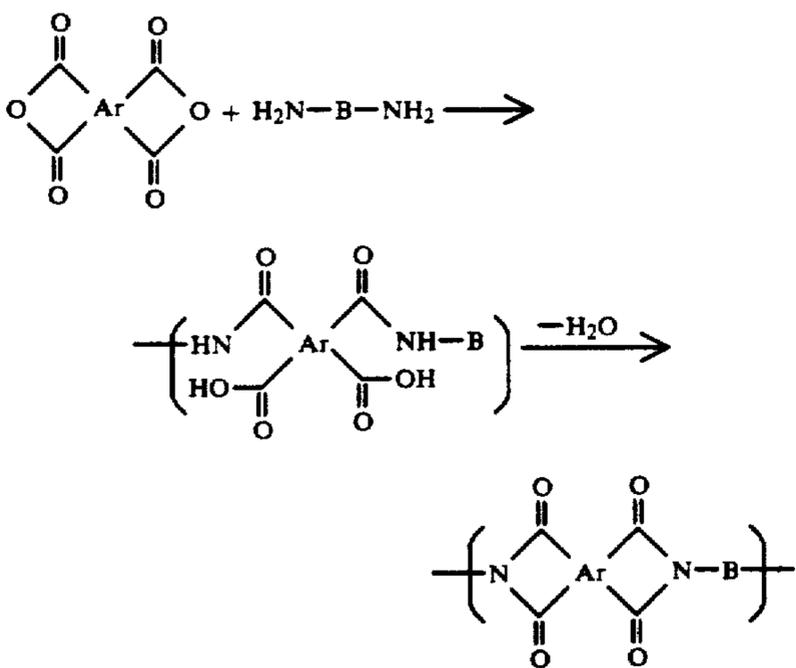
### BACKGROUND OF THE INVENTION AND INFORMATION DISCLOSURE STATEMENT

A class of polymers known as polyimides has become known for its combination of good heat stability and high upper use temperatures, as measured by glass transition temperature. A particularly useful type of such polyimides is known as polyimidesiloxanes.

Because of their combination of properties, polyimidesiloxanes have been used in electronic applications, particularly in microelectronic components in the integrated circuit industry.

Because many of the previously known polyimidesiloxanes are insoluble or difficultly soluble in solvents, when used in the microelectronics industry, there is a great need for polyimidesiloxanes having improved solubility characteristics, as well as a better balance of heat resistance and upper use temperature.

The chemistry for making polyimides has been well-known since about 1960. A structurally simple polyimide can be prepared by reacting a diamine with a dianhydride.



The first step, or the polycondensation reaction, generates polyamide acids which are hydrolytically unstable even at room temperature. The second step, or the imidization reaction, produces the stable polyimides desired for various applications.

Polyimidesiloxanes can be prepared by reactions employing siloxane diamines or siloxane dianhydrides with organic comonomers. Polyimidesiloxanes can also be prepared from siloxane diamines and siloxane dianhydrides without an organic comonomer.

The first polyimidesiloxane was prepared by reacting pyromellitic dianhydride (PMDA) with 1,3-bis-(amino-propyl)-1,1,3,3-tetramethyl disiloxane in 1966 (see V. H. Kuckertz, *Macromol. Chem.* 98, 1966, pp. 101-108). This polyimidesiloxane is a crystalline material and cannot be cast into flexible films from solvent. Polyimidesiloxanes derived from reactions of benzo-

phenone tetracarboxylic dianhydride (BTDA) and  $\alpha,\omega$ -diamino organo-polysiloxanes were disclosed by General Electric in 1967 in U.S. Pat. No. 3,325,450. Polyimidesiloxanes containing an  $\alpha,\omega$ -diamino organo-polysiloxane and a diether dianhydride (DEDA) have also been disclosed in U.S. Pat. No. 3,847,867.

All these BTDA and DEDA containing polyimidesiloxanes are amorphous materials. They have a glass transition temperature of no more than 100° C. and, therefore, have very limited upper use temperatures, despite the excellent thermal stability of these polymers up to about 200° C.

Polyimidesiloxanes containing both organic and siloxane monomers have been reported for PMDA containing copolymers (see Japan Kokai Tokkyo Koho 83/7473 and 83/13631); for BTDA containing copolymers (U.S. Pat. Nos. 3,553,282 and 4,404,350) and for diether dianhydride containing copolymers (U.S. Pat. No. 3,847,867). These PMDA containing polyimidesiloxanes are not soluble in any solvent. The BTDA containing polyimidesiloxanes are only soluble in high boiling or toxic solvents such as 1-methyl-2-pyrrolidinone, commonly known as N-methyl pyrrolidone (NMP), phenol or cresol, and the like. The diether [dianhydride] dianhydrides containing polyimidesiloxane, in addition, are also soluble in chlorinated solvents such as dichlorobenzene and dichloromethane. Since these phenol and chlorinated compounds are both corrosive and highly toxic, the polyimidesiloxanes have limited application in coating applications, especially in heat sensitive electronic devices. This is also due to the fact that a NMP soluble polyimidesiloxane normally has to be heated to 350° C. for at least half an hour to remove all the residual solvent in a film having a micron-thickness [film].

Only a few polyimidesiloxanes are soluble, even in high boiling and relatively toxic solvents, such as 1-methyl-2-pyrrolidinone (NMP), despite the fact that most of their polyamide acids are soluble. The usage of polyamide acids in coating applications has many drawbacks. First, a subsequent imidization reaction on substrates produces water. Therefore, it can only be used in very thin film coatings and where void-free property is not critical to performance. Second, the removal of high boiling, polar solvents, such as NMP, requires temperatures as high as 350° C. for about 30 minutes even for films of a micron thickness. This drying process is not only energy intensive, but also unacceptable to some heat sensitive electronic devices or substrates. In addition, the polyamide acids solution has to be stored at refrigeration temperature (>4° C.) and it still has a very short shelf life (about 3 months). Finally, only the fully imidized polyimidesiloxanes are thermally stable for melt processing such as extrusion and injection molding. A soluble polyimidesiloxane can be fully imidized at temperatures of about 160° to 170° C. in a solvent, whereas imidization for insoluble polyimidesiloxanes in the solid state may require temperatures 50° C. above their glass transition temperatures which can be as high as 200° to 250° C. Shaping not fully imidized polyimidesiloxanes by the melt processing method produces voids in the products and often is not desirable.

A variety of organic dianhydrides have been used in making soluble polysiloxaneimides. Some of these dianhydrides are disclosed in my copending applications as follows.

My copending application Ser. No. 239,372, filed Sept. 1, 1988, now U.S. Pat. No. 4,973,645, as a continuation-in-part of Ser. No. [032,722] 032,272, filed Mar. 31, 1987, and now abandoned, discloses that fully imidized polyimidesiloxanes made from oxydiphthalic anhydrides are soluble in solvents such as diglyme, tetrahydrofuran and methyl ethyl ketone.

My copending application Ser. No. 154,168, filed Feb. 9, 1988, now U.S. Pat. No. 4,829,131, discloses that substantially fully imidized polyimidesiloxanes made from a mixture of a biphenyl tetracarboxylic dianhydride and a benzophenone tetracarboxylic dianhydride are soluble in solvents such as diglyme, tetrahydrofuran and methyl ethyl ketone.

My copending application Ser. No. 153,898, filed Feb. 9, 1988, now U.S. Pat. No. 4,853,452, discloses that substantially fully imidized polyimidesiloxanes made from a bis(dicarboxyphenyl)hexafluoropropene dianhydride and mixtures with other dianhydrides are soluble in solvents such as diglyme, tetrahydrofuran and methyl ethyl ketone.

My copending application Ser. No. 205,412, filed June 10, 1988, now U.S. Pat. No. 4,956,437, discloses that substantially fully imidized polyimidesiloxanes made from sulfurdiphthalic anhydride are soluble in solvents such as diglyme, tetrahydrofuran and methyl ethyl ketone.

U.S. Pat. No. 4,535,099 describes a polyimide prepared from the reaction of an organic tetracarboxylic acid or derivative thereof with a mixture of an aromatic diamine and an amine-terminated silicone. Disclosed as suitable diamines are diamine pyridines, which are diprimary monotertiary amines. The polyimides are particularly useful in the preparation of flexible foams.

The above-noted U.S. Pat. No. 3,553,282 discloses making polyamic acids that may include 2,6-diaminopyridine. The patent does not teach how to make fully imidized and soluble polyimidesiloxanes. More specifically, the patent does not teach how to make a fully imidized, yet soluble, polyimidesiloxane from 2,6-diaminopyridine and dianhydrides such as BTDA and 6FDA.

A purpose of the present invention is to make novel polyimidesiloxanes.

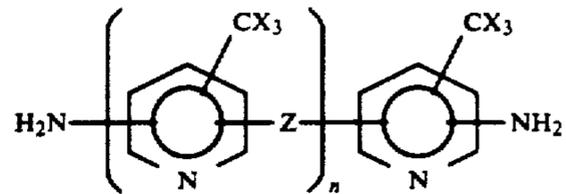
Another purpose of the present invention is to develop a fully imidized polyimidesiloxane which is soluble in low boiling, non-polar and non-toxic solvent such as diglyme. Another purpose of the present invention is to develop the desirable polyimidesiloxanes based on less expensive and readily available organic monomers. Another purpose of the present invention is to develop less expensive polyimidesiloxane which can be readily scaled-up into commercially available, large scale production. Another purpose of the present invention is to develop less expensive polyimidesiloxanes which can be used in price sensitive applications or in favorable competitive performance/cost positions in cable jacket, as well as 3D molded wire board applications and where high volume and low price are essential.

Another purpose of the invention is to provide fully imidized polyimidesiloxanes which are soluble not only in high boiling solvents, such as NMP, but also in low boiling, low toxic, less polar solvents such as diglyme or tetrahydrofuran (THF). A further purpose of the invention is to provide polyimidesiloxanes that have a good balance of heat resistance and high upper use temperatures, as measured by glass transition temperatures.

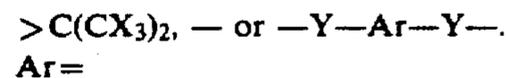
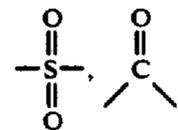
Another purpose of this invention is to produce curable and cross-linked polyimidesiloxanes.

#### SUMMARY OF THE INVENTION

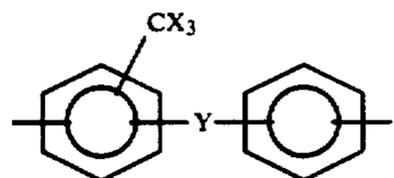
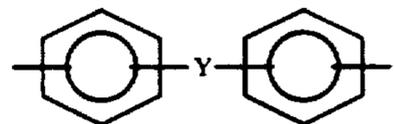
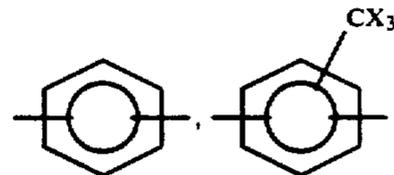
The invention relates to polysiloxaneimides that are prepared from compounds of the formula:



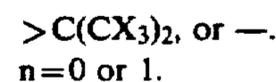
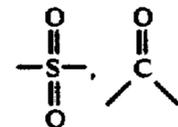
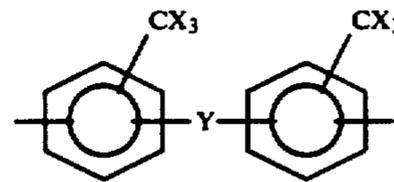
wherein X is hydrogen, halide, phenyl or combinations thereof,



Ar =



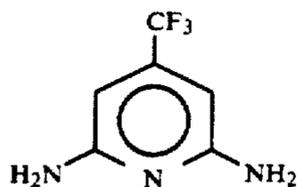
or



n = 0 or 1.

More specifically, the invention relates to polyimidesiloxanes that are prepared from 2,6-diamino-4-trifluoromethyl pyridine (2,6,4-DATF) which has the formula

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These diamino pyridine compounds are useful in making polyimidesiloxanes that have high glass transition temperatures and good thermal stability. Substantially fully imidized polyimidesiloxanes which are prepared from the foregoing pyridine compounds are soluble in diglyme which gives them particular utility in the micro-electronics industry. The latter polymers are prepared from the diamine, a difunctional siloxane monomer and an organic dianhydride. The above-described diamino pyridines, which are diprimary amines, can be used in admixtures with other diamines such as the tolylene diamine. Various organic dianhydrides can be used such as oxydiphthalic anhydride, sulfurdiphthalic anhydride, benzophenone tetracarboxylic dianhydride, the biphenyl tetracarboxylic dianhydrides, bis(dicarboxyphenyl)hexafluoropropene dianhydride, and diether dianhydrides.

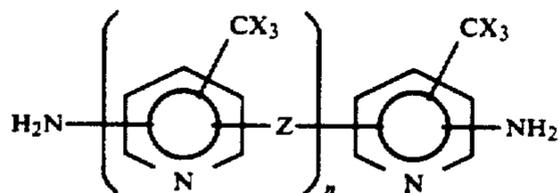
The polyimidesiloxanes of the invention can also be prepared with functional groups which render them directly curable. The polyimidesiloxanes can also be prepared with functional groups which when reacted with an unsaturated compound renders the polymers curable.

The products of the invention can be used in the form of solutions in the micro-electronic industry. The polymers can also be used in wire and cable coating and to prepare films, fibers, and molded and extruded articles.

DETAILED DESCRIPTION OF THE INVENTION

The Organic Diamine

The organic diamine component of the polyimidesiloxanes of the invention is the compound of the formula



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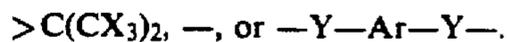
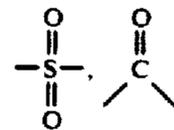
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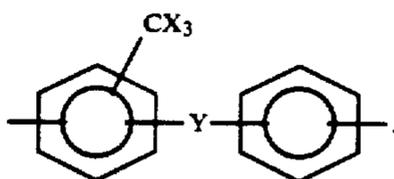
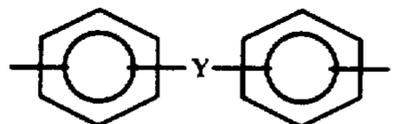
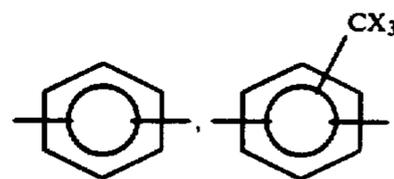
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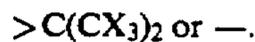
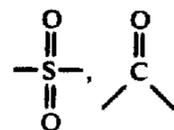
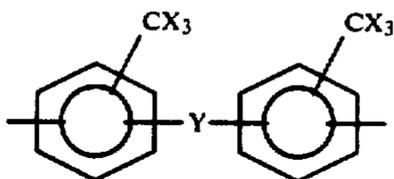
wherein X is hydrogen, halide, phenyl or combinations thereof



Ar =

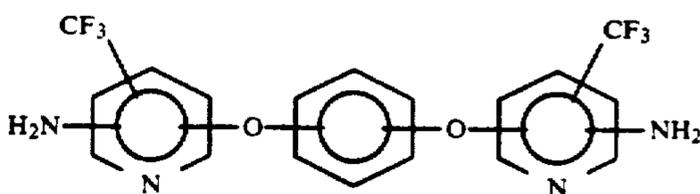
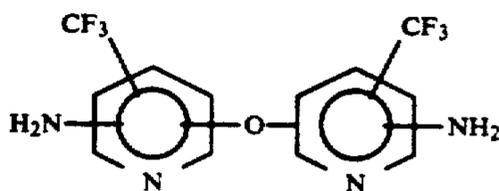


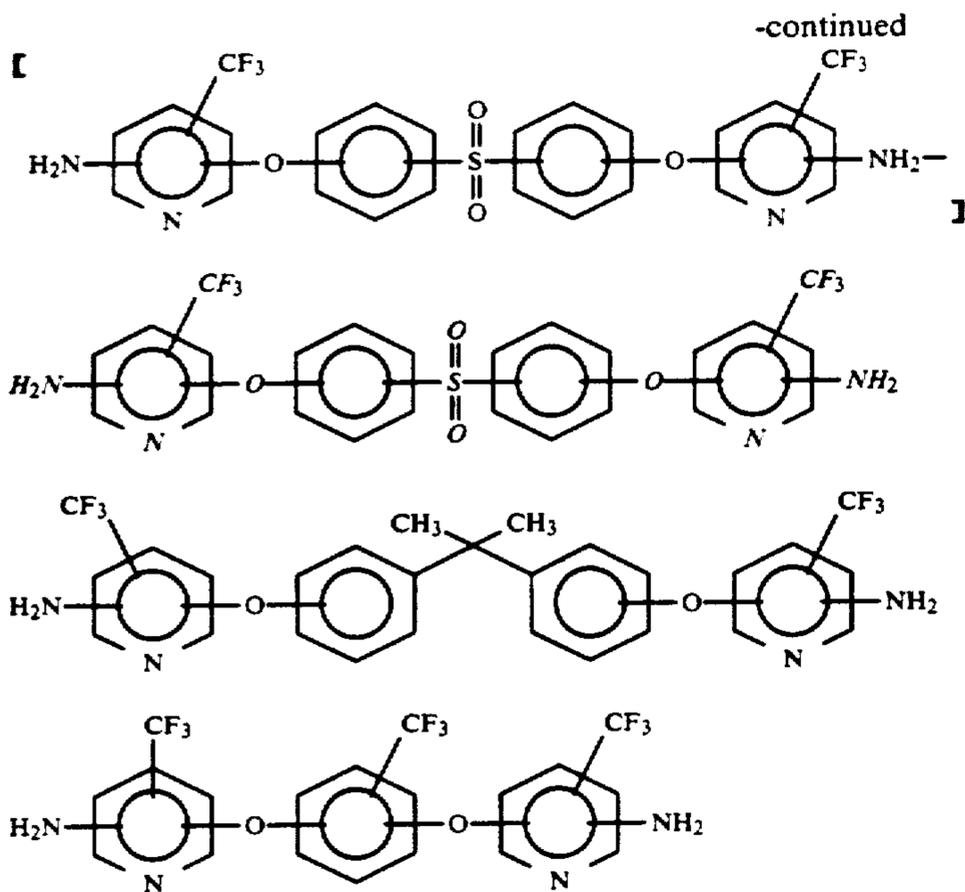
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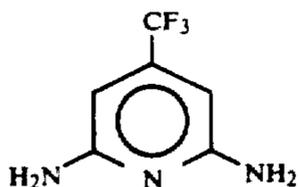
n = 0 or 1.

Examples of useful compounds of the above generic formula are as follows [...]:





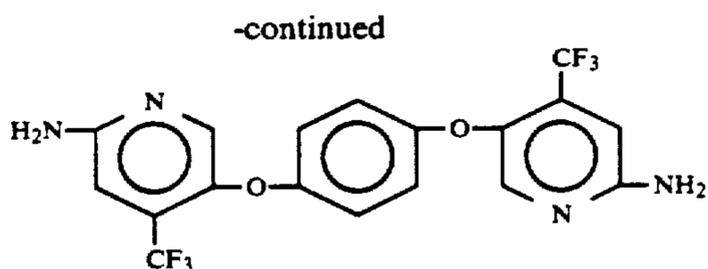
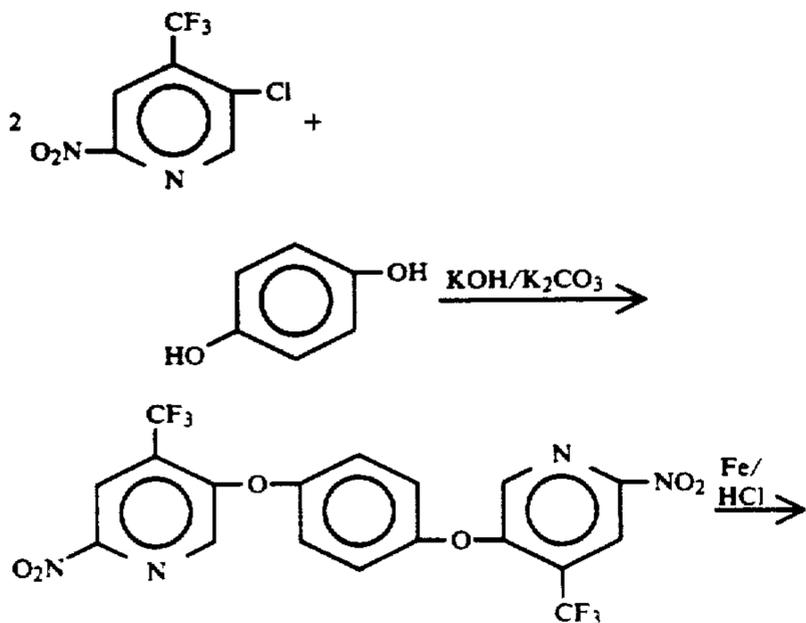
The preferred compound is 2,6-diamino-4-trifluoromethyl pyridine (2,6,4-DATF), which has the formula



The preparation of compounds with  $n=1$ ,  $Ar=$

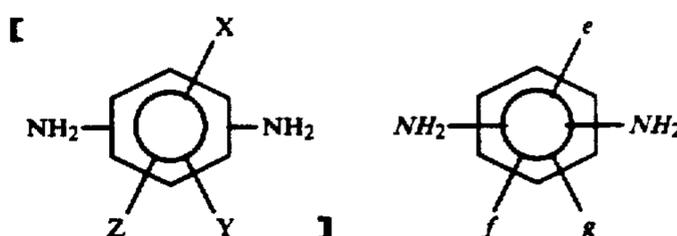


and  $Z = [O] -O-$  can be achieved, for instance, by the following reaction schemes:



It has been found that diamines that provide asymmetrical structure in the polyimidesiloxane chains are useful in combination with the amines such as 2,6,4-DATF, in making polyimidesiloxanes with the desirable and superior properties of this invention.

Other suitable diamines that provide asymmetrical structure in the polyimidesiloxane chain have the following formula:

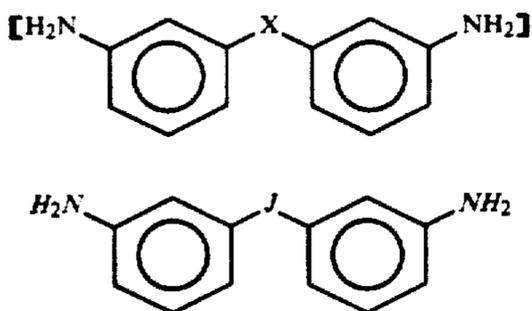


where  $[x, y$  and  $z]$   $e, f,$  and  $g$  are independently selected from hydrogen, halogen, alkyl or halogenated alkyl of 1 to 12 carbon atoms or aryl or halogenated aryl of 6 to 12 carbon atoms, provided that all of  $[x, y$  and  $z]$   $e, f,$  and  $g$  are not hydrogen. The preferred diamines have at least one alkyl substituent having at least one carbon atom.

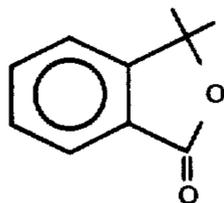
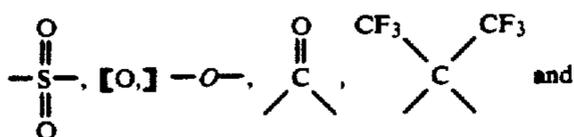
- Examples are:
- 2,4-tolyldiamine
  - 2,5-tolyldiamine
  - 2,6-tolyldiamine
  - m-xylyldiamine
  - 2,4-diamine-5-chloro toluene
  - 2,4-diamine-6-chloro toluene
  - trifluoromethyl-2,4-diaminobenzene
  - 2,4,6-trimethyl 1,3-diaminobenzene

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Other useful diamine compounds that are asymmetrical in the polymer chain include compounds with the formula:



wherein [X] J is  $-\text{CH}_2-$ ,



Examples are:

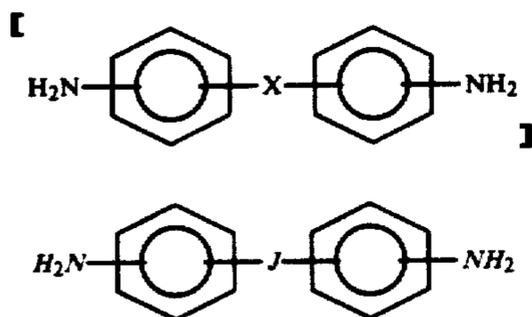
- m,m-methylene dianiline
- m,m-sulfone dianiline
- o,m-sulfone dianiline.

Another suitable diamine that is asymmetrical in the polyimidesiloxane is diaminoanthraquinone.

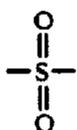
An especially preferred diamine is a mixture of 2,4-tolyldiamine and 2,6-tolyldiamine, especially the commercially available mixture of about 80 weight percent 2,4-tolyldiamine and about 20 weight percent 2,6-tolyldiamine.

Small amounts up to about 25 weight percent of diamines that are not [assymetrical] *asymmetrical* in the polymer chain can be employed in the polyimidesiloxane compositions. Such other diamines are disclosed in U.S. Pat. Nos. 4,395,527 and 4,586,997, the disclosures of which are incorporated herein by reference.

Such auxiliary diamines have the formula

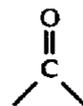


wherein [X] J is preferably



for retaining solubility in diglyme, THF or MEK. In addition, [the x] J can also [b] be

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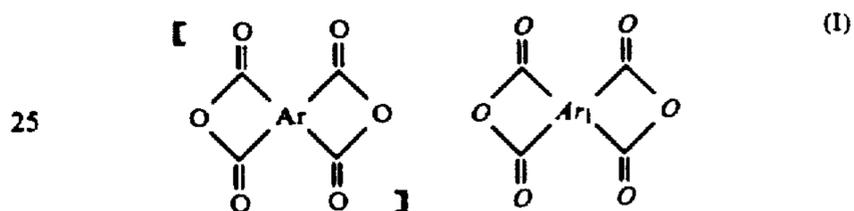
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$-\text{O}-$ ,  $-\text{S}-$  and  $-\text{CH}_2-$  for achieving only solubility in NMP. Additional organic diamines can be employed in much smaller quantities without affecting the favorable combinations of thermal stability glass transition temperature and solubility.

The Organic Anhydrides

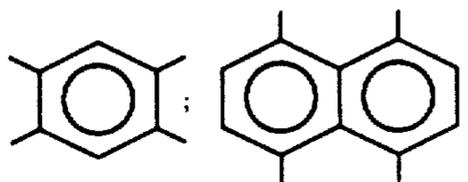
The present invention is based on the discovery that the use of the above-described diamines (typified by 2,6,4-DATF) when reacted with organic dianhydrides provide fully imidized polyimidesiloxanes which have a unique combination of solubility and thermal properties.

Useful organic dianhydrides include compounds having the following general formula:

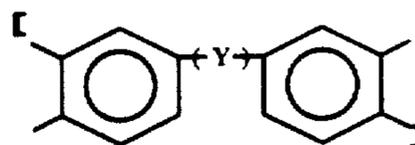


wherein [Ar] Ar<sub>1</sub> is

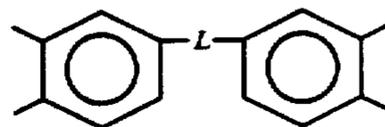
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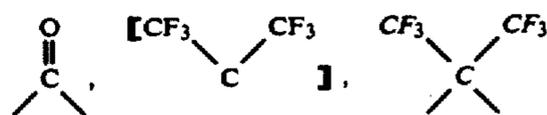
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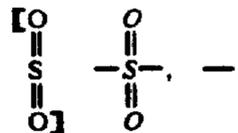
wherein [Y] L is [O]  $-\text{O}-$ ,

50



55 [C<sub>n</sub>H<sub>2n</sub>, S,]  $-\text{CH}_2-$ ,  $-\text{S}-$ ,

60



Other examples of such other dianhydrides are disclosed in U.S. Pat. Nos. 4,395,527 and 4,586,997, the disclosures of which are incorporated herein by reference. However, even though the incorporation of these dianhydrides may alter only slightly the solubility of the resulting polyimidesiloxanes in NMP or diglyme, these modified polyimidesiloxanes may become insoluble in

65

solvents, such as MEK or THF. This limits their applications where a very low boiling, non-toxic solvent such as MEK is required. In addition, the incorporation of the diether dianhydrides (DEDA), also reduces the glass transition temperature and thermal stability of polyimidesiloxanes of the invention and limit their upper use temperatures.

Preferred organic anhydrides that can be used in the practice of the invention include:

Oxydiphthalic anhydrides (ODPA), such as disclosed in Ser. No. [9,372] 239,372, filed Sept. 1, 1988, now U.S. Pat. No. 4,973,645, the disclosure of which is incorporated herein by reference;

Sulfurdiphthalic anhydrides (SDPA), such as disclosed in Ser. No. [5,412] 205,412, filed June 10, 1988, now U.S. Pat. No. 4,956,437, the disclosure of which is incorporated herein by reference;

Sulfonediphthalic anhydrides;

Benzophenone tetracarboxylic dianhydride (BTDA);

Biphenyl tetracarboxylic dianhydrides (BPDA);

Bis(dicarboxyphenyl)-hexafluoropropene dianhydride, (6FDA);

Diether dianhydrides (DEDA); such as disclosed in U.S. Pat. No. 4,395,527, the disclosure of which is incorporated herein by reference.

Mixtures of the foregoing anhydrides can also be employed. Particularly useful are the following mixtures of anhydrides:

BPTA and BTDA

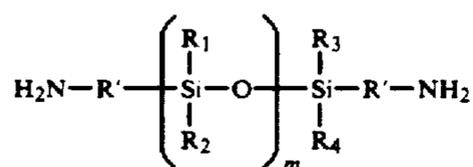
6FDA and ODPA

6FDA and BPDA

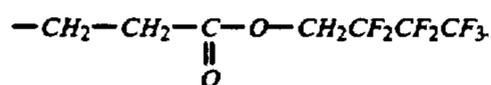
BTDA and ODPA.

The Siloxane Monomers

Siloxane diamino compounds that can be used for the present invention have the following formula:



wherein  $m$ , the average number of repeating units, is 1 to about 200, and  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ , and  $\text{R}_4$  are independently selected from a substituted or unsubstituted aliphatic mono-radical of 1 to 12 carbon atoms or substituted or unsubstituted aromatic mono-radical of 6 to 10 carbon atoms. Suitable radicals include  $-\text{CH}_3$ ,  $-\text{CF}_3$ ,  $[-(\text{CH}_2)_n\text{CF}_3]$ ,  $-(\text{CH}_2)_a\text{CF}_3$ ,  $-\text{C}_6\text{H}_5$ ,  $-\text{CF}_2-\text{CHF}-\text{CF}_3$  and  $[-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{O}-\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_3]$

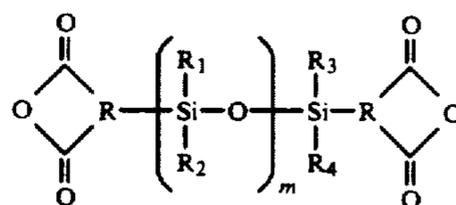


$\text{R}'$  is a di-radical of the foregoing type (i.e.,  $\text{R}'$  is defined the same as  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ , or  $\text{R}_4$  but is a di-radical instead of a mono-radical). Suitable di-radicals include  $[-(\text{CH}_2)_n-(\text{CF}_2)_m-(\text{CH}_2)_n(\text{CF}_2)_m]$ ,  $-(\text{CH}_2)_a$ ,  $-(\text{CF}_2)_a$ ,  $-(\text{CH}_2)_a(\text{CF}_2)_b$ , and  $-\text{C}_6\text{H}_4-$ , wherein  $[m$  and  $n]$   $a$  and  $b=1$  to 10.

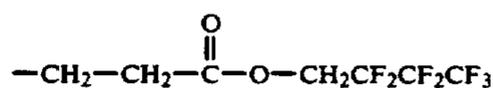
The employment of an  $\alpha, \omega$ -diaminosiloxane is important for achieving the desired solubility in diglyme, THF or MEK in the present invention. The siloxane diamine also provides the flexibility or resilience of the polyimidesiloxanes at low temperatures, especially when the  $m$  is an integer of more than about 5, or prefer-

ably more than about 7. When the  $m$  is more than about 50, the incorporation of diaminosiloxane into the polyimidesiloxane becomes difficult even though it is not impossible; and a dual solvent system (one polar and one non-polar solvent) for copolymerization may have to be employed. In general, the employment of the  $\alpha, \omega$ -diaminosiloxane and  $\alpha, \omega$ -dianhydride siloxane are interchangeable in the present invention. However, for making polyimidesiloxanes of high glass transition temperature, the mole percent of the mixture of dianhydrides in the total dianhydride should be maximized; and therefore, it is more desirable to employ the combination of the organic dianhydride with an organic diamine and an  $\alpha, \omega$ -diaminosiloxane.

Siloxane dianhydrides which can be incorporated instead of or in addition to the siloxane diamines for the practice of the present invention can have the formula:



wherein  $m$  is hereinbefore defined,  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  are independently selected from a substituted or unsubstituted aliphatic mono-radical of 1 to 12 carbon atoms or substituted or unsubstituted aromatic mono-radical of 6 to 10 carbon atoms. Suitable radicals include  $-\text{CH}_3$ ,  $-\text{CF}_3$ ,  $[-\text{CF}_2-\text{CHF}-\text{CF}_3]$ ,  $-(\text{CH}_2)_a\text{CF}_3$ ,  $-\text{CF}_2-\text{CHF}-\text{CF}_3$ ,



and  $-\text{C}_6\text{H}_5$ .

$\text{R}$  is a tri-radical of the foregoing type (i.e.,  $\text{R}$  is defined the same as  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ , or  $\text{R}_4$  but is a tri-radical instead of a mono-radical). Suitable tri-radicals include  $-\text{CH} <$ ,



It is also well-known to those skilled in the art that when the  $\text{C}_6\text{H}_5-$  or  $\text{CF}_3\text{CH}_2-\text{CH}_2-$  group is used in the siloxane block, in replacement of the  $-\text{CH}_3$  group, the solubility of resulting polyimidesiloxanes in chlorinated solvents, such as  $\text{CH}_2\text{Cl}_2$  and ether solvent such as diglyme and THF will increase. In addition, the polyimidesiloxane copolymers consist of phenylated siloxane block, or fluorinated siloxane block will also have higher thermal stability. This is due to the fact that the least thermally stable groups in the polyimidesiloxanes is the  $-\text{CH}_3$  group on the siloxane block. Accordingly, without showing specific examples one can expect that polyimidesiloxanes of the present invention can be further improved by incorporating the  $[\text{C}_6\text{H}_5]$   $\text{C}_6\text{H}_5-$  group or  $[\text{CF}_3\text{CH}_2]$   $\text{CF}_3\text{CH}_2-\text{CH}_2-$  group

into their siloxane blocks in order to improve their solubility and thermal stability.

When various dianhydrides are employed, their solubility in various solvents, glass transition temperatures and thermal stability changes depending on the chemical nature of these co-monomers. For instance, when a siloxane dianhydride is incorporated in the presence of a dianhydride, the solubility of the polymer increases, while the glass transition temperature and thermal stability will be lowered. Therefore, depending on the requirements for applications, the incorporation of siloxane dianhydride may become unfavorable. On the other hand, when an organic dianhydride such as PMDA is added in small proportions of less than 5 mole percent, the resulting polyimidesiloxanes still has the desirable solubility in, for instance, NMP. The incorporation of PMDA can increase the glass transition temperature and thermal stability of the resulting polyimidesiloxanes, and, therefore, can provide more favorable products for extrusion or injection molding applications. However, one may also find that even with a small amount of PMDA in the polyimidesiloxanes, the resulting copolymers may become insoluble in solvents, such as diglyme, THF or MEK, and their applications as coating materials will be limited, for instance, in heat sensitive electronic devices or substrates.

#### The Process For Soluble Polyimidesiloxanes

Although the chemistry for reactions of organic diamines with organic dianhydrides has become well-known, the preparation of polyimidesiloxanes in the presence of the siloxane comonomers may sometimes require special techniques. For instance, when the repeating unit  $m$ , of the siloxane monomer is larger (i.e.,  $<20$  to  $40$ ), it may be desirable to use a dual solvent system: i.e., a solvent system consisting not only of a polar solvent, but also a less polymer solvent. (See, for instance, McGrath et al., *Polymer Preprints*, 27 (2), 1986, pp. 403). It is also known that in the practice of making soluble polyimides, if a polyimide is soluble in a given solvent, in which the polyamide acid is not soluble, one can prepare the polyimide directly in a one step polymerization process, that is, by a simultaneous imidization and polycondensation process, referred to as the one-step process. This procedure can be advantageous, especially when a desirable polymer solution for coating applications has to be made out of a given solvent in which the polyamide acids are not soluble. The problem with the simultaneous imidization and polycondensation is that the depolymerization of the polyamide acid in the presence of the water which is produced during the imidization step, can be very severe. Theoretically, the depolymerization can become an irreversible process, since it produces a dicarboxylic acid and an amino compound. The carboxylic acid reacts with amino compounds at much higher temperatures as compared to the almost instantaneous reaction of the dianhydrides with the amino compounds at room temperature. The depolymerization of polyamide acids can become very severe at high temperatures. This one-step process often produces polyimidesiloxanes with much lower molecular weight as compared to those produced in a good solvent, in which the polyamide acid and the imidized polymers are both soluble, and one employs a two-step process. The two-step process employs a low temperature polycondensation step which generates very high molecular weight polyamide acid and then a very fast

heating step to imidize and remove water generated from imidization.

The two-step process produces higher molecular weight materials which have higher thermal stability and mechanical strength, especially higher elongation at break. The polycondensation temperature for the two-step process should be below  $60^{\circ}\text{C}$ ., preferably below room temperature. The imidization can be carried out at temperatures from  $90^{\circ}\text{C}$ . to  $180^{\circ}\text{C}$ ., or the refluxing temperature of the solvents. When the boiling temperature of the desirable solvent for imidization is below  $160^{\circ}\text{C}$ ., the use of dehydrating agents and/or a base catalyst is desirable. A suitable dehydrating agent is acetic anhydride. The catalyst is a tertiary amine, such as pyridine. When the acetic anhydride is employed, lower imidization temperatures can be employed to complete the imidization. In addition, an azeotropic agent with water can also be added to the reactor. The use of an azeotropic agent such as toluene can facilitate the removal of water presented in the reactor and minimize the depolymerization of the polyamide acids. When an azeotropic agent is employed, a continuous recovery of fresh azeotropic agent can be achieved by using also a Dean Stark trap under the condenser.

The degree of polycondensation is important for obtaining good thermal and mechanical properties in making polyimidesiloxanes. The reaction time for making high molecular weight polyimidesiloxanes is normally several times longer than that required for making polyimides due to the fact that the reactivity of the  $\alpha,\omega$ -diamino or dianhydride siloxanes is normally lower than organic monomers. In general, the high molecular weight siloxane monomers react much slower than the organic monomers in a polar solvent. Accordingly, one can also expect that the microstructure of the polyimidesiloxane depends not only on the molar ratio of the organic to siloxane monomers (or the composition of the monomers), but also on the additional sequence of these monomers during polycondensation. For instance, when a high molecular weight  $\alpha,\omega$ -diamino siloxane is employed, one sometimes finds that it is advantageous to first react the organic dianhydride without the presence of the organic diamine. This procedure not only can overcome the need of using a dual solvent system, but also can result in a much more uniform and controllable polyimide block size and distribution. Compared to a polyimidesiloxane with identical chemical make-up, but prepared with a different addition sequence (i.e., add all monomer together into a solvent at once) the polyimidesiloxane with more uniform and controlled imide size and distribution have a more soluble characteristic toward siloxane-like solvent or non-polar solvent. On the other hand, polyimidesiloxanes have the identical number average molecular weight of imide-block but having a broad molecular weight distribution will be less soluble in the diglyme or THF.

Depending on the property requirements for various applications, one can therefore design polyimidesiloxanes by their composition, but also control their microstructures through monomer addition sequence for one's advantage.

The solvents that can be used for the polymerization of the present invention are the phenol solvents;  $N,N$ -dialkylated carboxylamide solvents and monoalkylated or dialkylated ether type solvents. The examples of phenol solvents are phenol, *o*-cresol, *m*-cresol, *o*-chlorophenol, *m*-chlorophenol, *p*-fluorophenol, 2,4,6-

tribromophenol; examples of N,N-dialkylated carboxylamide solvents are N,N-dimethylformamide, N,N-dimethylacetamide, NMP; ether type solvents are tetrahydrofuran (THF), diglyme or triglyme. Other solvents, such as  $\gamma$ -butyrolactone, sulfolane, dimethylsulfide and chlorinated benzenes such as p-dichloro benzene which are commonly mentioned in various polyimide patents can also be used.

Polyimidesiloxane can also be prepared in a melt polymerization process; especially when the glass transition temperature of the imide block is lower than say about 200° C.; or a large proportion (>25%) of the siloxane comonomers is employed. In practice, the melt polycondensation can be done in an extruder in which imidization can be achieved using a vented zone situated close to the outlet nozzle.

To achieve high molecular weight polyimidesiloxanes, the total moles of dianhydride component(s) should equal the total moles of diamine component(s). To reduce the molecular weight an excess of dianhydride, diamine components or small amounts of monofunctional compounds can be employed.

When the siloxane monomer is a diamine, for every 1 mole of siloxane diamine employed, assume that n moles of organic diamine is employed. Then [n+1] c+1 moles of organic dianhydride is employed.

When the siloxane monomer is a dianhydride, for every 1 mole of siloxane dianhydride employed, assume that [n] c moles of organic dianhydride is employed. Then [n] c+1 moles of organic diamine must be employed.

In the foregoing cases, [n] c has a value of greater than 0.01 but no more than 40, preferably 20.

When [0.01 ≤ n ≤ 0.1] 0.01 ≤ c ≤ 0.1, the [polyimidesiloxane] polyimidesiloxanes exhibit elastomeric or rubber properties and are useful for potting, encapsulation, and sealing applications. Especially, a cross-linking elastomeric polyimidesiloxane will have great value in the above-mentioned applications. When [0.1 ≤ n ≤ 10] 0.1 ≤ c ≤ 10, polyimidesiloxanes with thermoplastic elastomeric properties are obtained. These materials are useful for wire, cable, injection molding and protective coating applications. When [10 ≤ n ≤ 40] 10 ≤ c ≤ 40, very high strength and rigid thermoplastics are produced which are useful for molding and coating applications.

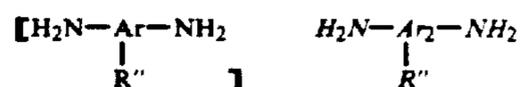
#### The Curable Polyimidesiloxanes

The soluble polyimidesiloxanes described above have many valuable properties and uses. However, limitations are found in their applications, especially in areas where higher chemical or creep resistance are desirable or even critical. For instance, most of the polyimidesiloxanes show limited hydraulic fluid or jet fuel resistance when their siloxane content is over 30 to 40%. Even though this weakness can be largely reduced by incorporating fluorinated compound into their backbone structure, in particular, into their siloxane blocks, it is still more desirable to convert these fluorinated polyimidesiloxanes into thermosets in order to achieve higher solvent and creep resistance. In general, when a cross-linkable polyimidesiloxane carries an acrylic functionally, it can be cured by either thermal or photomethod. A photosensitive or photocurable polyimidesiloxane is especially valuable for patterning applications in microchips or integrated circuit industries. Furthermore, these novel curable polyimidesiloxanes, as well as the soluble polyimidesiloxanes, can also find applications in passivation layer, alpha particle barrier, elec-

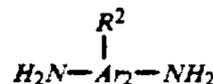
tron beam patterning, ion implant mask or interlayer dielectric in electronics and micro-electronic industries.

The polyimidesiloxanes of the invention can be made curable by the inclusion of reactants that have functionalities that are capable of being cross-linked, or that have intermediate functionalities that can be suitably modified with cross-linkable moieties after formation of the polymer. The required functionalities can be incorporated into the polymer of the invention by use of suitable diamines and/or siloxane compounds.

The diamine compounds have the characteristic described for the soluble polymers of a diamine that provide asymmetrical structure in the polyimidesiloxane chains. The diamines further have the following general formula:

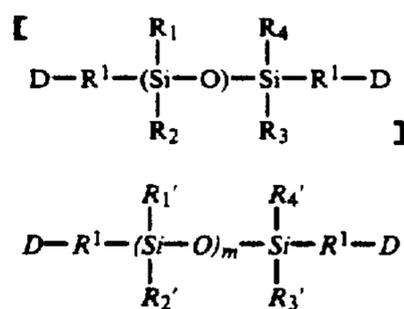


wherein [Ar] Ar<sub>2</sub> is aromatic, R'' is a hydroxyl, hydrothiol or carboxylic radical, preferably a hydroxyl or carboxylic radical. The metals salts of the carboxylic groups are also contemplated. Suitable metals are sodium and silver. The typical examples of these compounds are, for instance, 3,5-diaminobenzoic acid and 3,5-di-aminophenol, and the like. *Diamines that have functionalities that are capable of being cross-linked have the following formula*



where R<sup>2</sup> is at least one of an acrylic-, ethylenic- or an acetylenic-bearing radical.

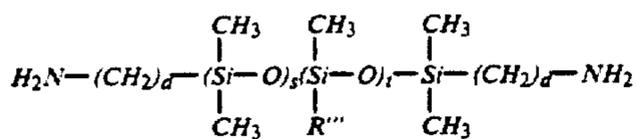
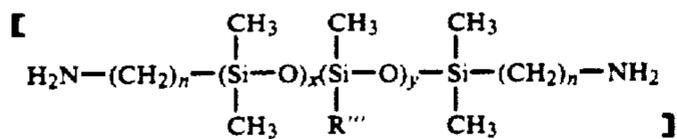
The functionalized siloxane diamines or dianhydrides have the following general structure:



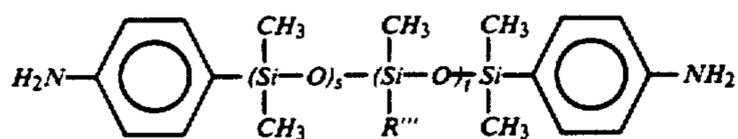
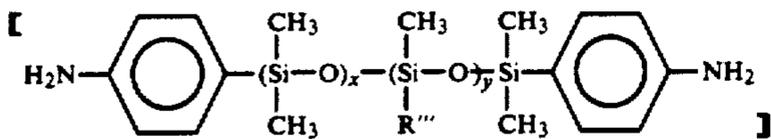
wherein m is hereinbefore defined, D is either an amino or anhydride group and the R<sup>1</sup> is a diradical R' or a triradical R, such as described hereinbefore. Radicals R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>' and R<sub>4</sub>' are the same as R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> [are] as described hereinbefore, except that one or more of [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can be] R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>' and R<sub>4</sub>' is a halogen, hydride (H), vinyl or a hydroxyl group, when D is an anhydride group [;], or vinyl or hydroxyl when D is an amino group.

In the functionalized siloxane diamine or dianhydride moieties, the [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub>] R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>' and R<sub>4</sub>' groups can also be selected from acetylenic-, ethylenic- or acrylic-groups as a result of reaction of moieties containing hydride (H), hydroxyl, halogen and halide groups with acetylenic-, ethylenic- or acrylic-bearing compounds, respectively, as described hereafter.

Examples of the functionalized siloxane  $\alpha,\omega$ -diamino compounds can be the following:

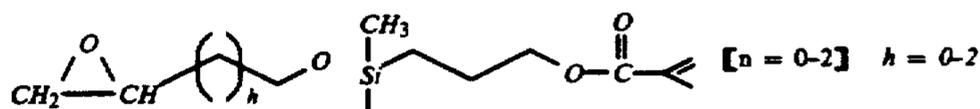
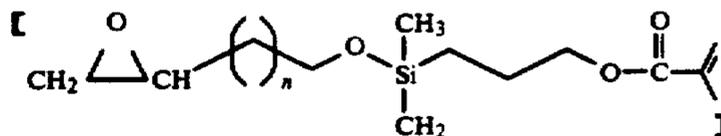
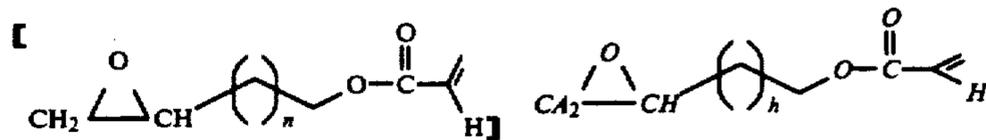
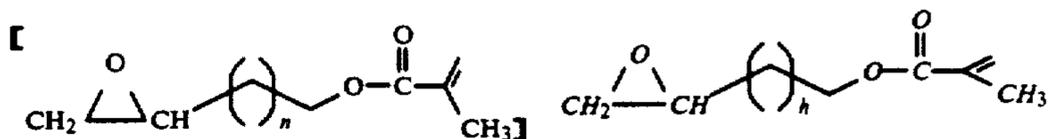
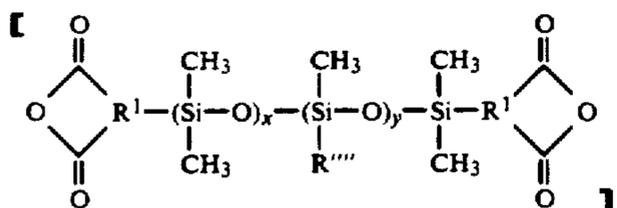


or

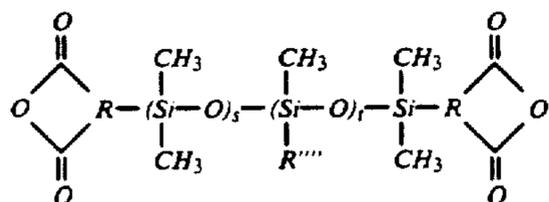
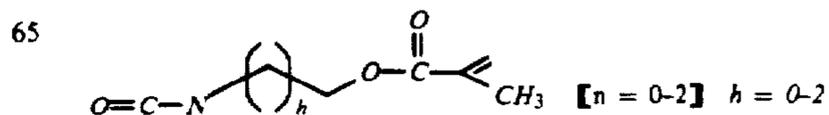
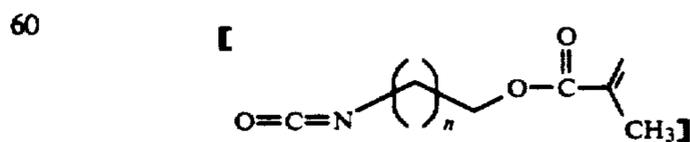


wherein  $[n]$   $d$  is an [integral] integer from 2 to 6, preferably 3 and 4; and  $\text{R}''''$  is a vinyl or hydroxyl group, and  $[x+y]$   $s+t=m=1$  to [100] 200, preferably 4-40 and  $[y]$   $t$  is an integer of 1 to 15, preferably 1 to 5.

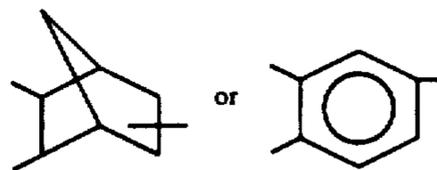
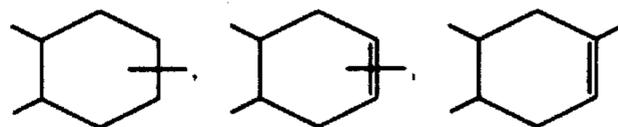
The examples of the functionalized dianhydride are:



or an isocyanate-bearing acrylate such as



where  $[\text{R}^1]$  is examples of  $\text{R}$  include



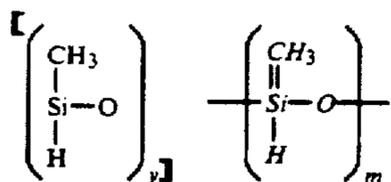
and  $\text{R}''''$  is selected from hydride (H), hydroxyl, halogen and vinyl groups, preferably the H and vinyl groups. The  $[x]$   $s$  and  $[y]$   $t$  have the same meanings as above.

The Process For Making Curable Polyimidesiloxanes

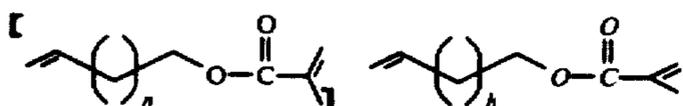
The procedures for making soluble polyimidesiloxanes are generally followed.

The comonomers are generally copolymerized in an appropriate solvent such as NMP or diglyme. The fully imidized, polyimidesiloxane which carries at least one kind of the functionalities described above, can then be further reacted or grafted with an acetylenic, ethylenic or acrylic-bearing compound to provide the final products desired for this invention. The grafting reaction is preferably conducted in a non-reactive solvent, preferably in diglyme, THF or MEK. Since there are many different functional groups that can be selected for the functionalized polyimidesiloxane, the grafting reaction desired for this invention has to be varied accordingly. For instance, when a carboxylic or hydroxyl-containing polyimidesiloxane is first prepared, the grafting of an acrylic group can be achieved by using either an epoxy-bearing acrylate such as the

When the functional group of the polyimidesiloxane is located in the siloxane blocks, the grafting reaction can be achieved using either an hydrosilylation reaction or a condensation reaction. For instance, when a



group is present in a polyimidesiloxane, the grafting can be achieved via hydrosilylation: i.e., reaction of a vinyl group with a Si—H group in the presence of a catalyst, such as a Pt catalyst. Therefore grafting of a



compound results in an acrylate-bearing polyimidesiloxane. When a —OH or epoxy group is present in the polyimidesiloxane, on the other hand, the grafting can be achieved via a condensation reaction. For instance, the reactions of an isocyanate-bearing acrylate or an acrylic acid or methacrylic acid with the hydroxyl or epoxy group on the polyimidesiloxane can result in an acrylic-bearing polyimidesiloxane desired for the present invention.

When an acetylenic-bearing compound also bears a carboxylic, an epoxy or isocyanato functionality, it is clear that the compounds can be grafted onto a polyimidesiloxane which carries an —OH or, a carboxylic group, respectively.

When an ethylenic group is present in the siloxane block of the polyimidesiloxane, it can be used as such, and further be cured thermally via free radical cross-linking reactions or can be further changed into polyimidesiloxanes which carry either an acrylic or an acetylenic group. The grafting reaction of this kind is difficult to achieve, however, due to the lack of appropriate chemicals.

To prepare the functionalized polyimidesiloxanes with a functional group presented in the imide block, it is preferred to start with an OH or —COOH-bearing diamino compound. On the other hand, this kind of siloxane monomer is usually not readily available. The incorporation of epoxy, silicone hydride or silicone hydroxyl group can be achieved via equilibration of the  $\alpha$ ,  $\omega$ -diamino or  $\alpha$ , $\omega$ -dianhydride siloxane with cyclic silicone epoxy, silicone hydride or silicone hydroxy compounds. In any event, it is preferred to graft the acrylic or ethylenic or acetylenic group rather than using an acrylic, ethylenic or acetylenic diamino or dianhydride compound for making the desired polyimidesiloxane. This is to avoid thermally cross-linking reactions of these functionalities during imidization of the polyimidesiloxane at high temperatures (about 160° to 170° C./2 hrs in solvent). A grafting reaction of a fully imidized polyimidesiloxane with the above described functionalities can be, in general, carried out at much lower temperatures. For instance, the hydrosilylation can be carried out at temperatures as low as 25° C. in the presence of a platinum catalyst. The condensation between the hydroxyl or carboxylic group with the epoxy group can be achieved at temperatures of no more than 120° C., within hours with the presence of a tertiary amine as a catalyst. In this invention, the pyri-

dine compound serves as the tertiary amine. The reaction of an hydroxyl or carboxylic group with an isocyanate group needs even lower temperatures (RT to 80° C.), and the like.

To avoid the need for isolation of the reaction product from solvent, it is desirable to conduct the grafting reaction in the solvent which is acceptable for coating operations. The desirable solvents of these kinds are solvents with low flammability and/or toxicity, such as diglyme or MEK. The latter has been widely employed in coating industries due to its low boiling temperature.

In this specification and claims halogen shall refer to fluorine, chlorine, bromine and iodine, but preferably to fluorine and chlorine. Aromatic generally refers to hydrocarbon aromatic.

In the following Examples and throughout the specification and claims, parts are by weight and temperatures are in degrees Celsius, unless indicated otherwise.

## EXAMPLES

### Example 1

Into a 50 ml flask was added 1.86 grams of 4,4'-oxydiphthalic anhydride (4,4'-ODPA), 0.71 gram of 2,6,-diamino-4-trifluoromethyl pyridine (2,6,4-DATF) and 1.68 grams of siloxane monomer G<sub>9</sub> and 20 milliliters of NMP. The mixture was reacted at room temperature for 16 hours. Then the solution was cast in a Teflon mold at 140° C. for four hours. The temperature was raised to 250° C. for ½ hour. The resulting polymer film was designated as (OF')<sub>2.0</sub>G<sub>9</sub>.

### Example 2

Example 1 was repeated using 1.76 grams of biphenyl tetracarboxylic dianhydride (BPDA), 0.71 gram of 2,6,4-DATF and 1.68 grams of siloxane monomer G<sub>9</sub>. The resulting polymer product was designated (B'F')<sub>2</sub>G<sub>9</sub>.

### Example 3

Example 1 was repeated using 1.96 grams of benzophenone tetracarboxylic dianhydride (BTDA), 0.71 gram of 2,6,4-DATF and 1.68 grams of siloxane monomer G<sub>9</sub>. The resulting polymer film was designated as (BF')<sub>2</sub>G<sub>9</sub>.

### Example 4

Example 1 was repeated using 2.66 grams of bis-(dicarboxyphenyl) hexafluoropropene dianhydride (6FDA), 0.71 gram of 2,6,4-DATF and 1.68 grams of siloxane monomer G<sub>9</sub>. The resulting polymer product was designated (FF')<sub>2</sub>G<sub>9</sub>.

### Example 5

Example 1 was repeated using 5.17 grams of ODPA, 2.82 grams of siloxane monomer G<sub>9</sub>, 1.09 grams of tolyl diamine (TDA) and 0.73 gram of 2,6,4-DATF. The resulting polymer films were designated as (TO<sub>0.5</sub>F'<sub>0.5</sub>)<sub>2</sub>G<sub>9</sub>.

### Example 6

Example 1 was repeated using 4.34 grams of ODPA, 3.38 grams of siloxane monomer G<sub>9</sub> and 1.22 grams of TDA. The resulting films are designated as (OT)<sub>2.5</sub>G<sub>9</sub>.

Example 7

Example 3 was repeated using 1.93 g of BTDA, 0.24 g of 2,6,4-DATF, 0.33 g of TDA and 1.68 g of siloxane monomer G<sub>9</sub>. The resulting polymer films were designated as (BF'<sub>0.5</sub>T<sub>0.5</sub>)<sub>2</sub>G<sub>9</sub>.

Example 8

Example 1 was repeated using 5.17 g of ODPa, 2.82 g of siloxane monomer G<sub>9</sub>, 0.81 g of TDA and 1.09 g of 2,6,4-DATF. The resulting polymer films were designated as (OF'<sub>0.5</sub>T<sub>0.5</sub>)<sub>2</sub>G<sub>9</sub>.

Example 9

Example 3 is repeated using 4.83 g of BTDA, 6.66 g of 6-FDA, 3.48 g of 2,6,4-DATF, and 8.40 g of siloxane monomer G<sub>9</sub>. The resulting polymer films are designated as (BF<sub>0.5</sub>F<sub>0.5</sub>)<sub>2</sub>G<sub>9</sub>.

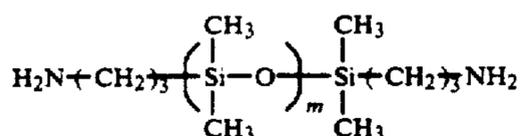
Example 10

Example 1 is repeated using 4.65 g ODPa, 4.83 g BTDA, 1.74 g of 2,6,4-DATF, 1.21 of TDA, and 8.40 g of siloxane monomer G<sub>9</sub>. The resulting polymer films are designated as (O<sub>0.5</sub>B<sub>0.5</sub>F'<sub>0.5</sub>T<sub>0.5</sub>)<sub>2</sub>G<sub>9</sub>.

Example 11

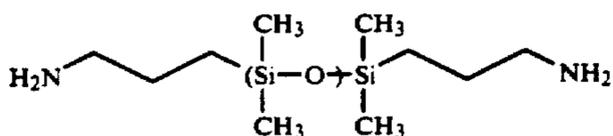
Example 1 was repeated using 9.66 g of BTDA, 2.44 g of TDA and 8.40 g of siloxane monomer G<sub>9</sub>. The resulting polymer films were designated as (BT)<sub>2</sub>G<sub>9</sub>.

In the foregoing examples, G<sub>m</sub> has the formula:

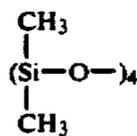


where m indicates the average number of repeating units, as shown in Table 1, for example, G<sub>8.75</sub>.

G<sub>9</sub> siloxane monomer is an equilibrium product of one mole of G<sub>1</sub> with 2 moles of D<sub>4</sub> at 87°-90° C. G<sub>1</sub> has the following structure:



and D<sub>4</sub> is the cyclic tetramer having the formula



In the formula, G has a nominal value of 9 units. Experimentally G has a value of about 8.75.

Solubility Tests and Results

Approximately 0.1 g of polysiloxaneimide films were added into 1 ml of diglyme. The mixture was heated to 60°-80° C./16 hours. The solubility of those films were summarized as follows:

Example No.	Structure	Solubility In NMP	Solubility In Diglyme
1	(OF') <sub>2</sub> G <sub>9</sub>	+	-
2	(BF') <sub>2</sub> G <sub>9</sub>	+	-
3	(BF) <sub>2</sub> G <sub>9</sub>	+	+

-continued

Example No.	Structure	Solubility In NMP	Solubility In Diglyme
4	(FF') <sub>2</sub> G <sub>9</sub>	+	+
5	(OT <sub>0.5</sub> F' <sub>0.5</sub> ) <sub>2</sub> G <sub>9</sub>	+	+
6	(OT) <sub>2.5</sub> G <sub>9</sub>	+	+*
7	(BF' <sub>0.5</sub> T <sub>0.5</sub> ) <sub>2</sub> G <sub>9</sub>	+	+
8	(OF' <sub>0.5</sub> T <sub>0.5</sub> ) <sub>2</sub> G <sub>9</sub>	+	+
9	(B <sub>0.5</sub> F <sub>0.5</sub> F') <sub>2</sub> G <sub>9</sub>	+	+
10	(O <sub>0.5</sub> B <sub>0.5</sub> F' <sub>0.5</sub> T <sub>0.5</sub> ) <sub>2</sub> G <sub>9</sub>	+	+
11	(BT) <sub>2</sub> G <sub>9</sub>	+	-

\*Precipitated out after standing at room temperature for 3 weeks.

A polyimidesiloxane that is soluble in diglyme can be prepared by copolymerization of benzophenone tetracarboxylic dianhydride (BTDA) and DATF with siloxane monomer (Example 3). A diglyme soluble polymer is also produced by substitution of a tolyldiamine for a portion of the DATF (Example 7). The resulting product has other useful properties such as high tear strength. It was also found that a polyimidesiloxane that is insoluble in diglyme and made by copolymerizing ODPa and DATF with a siloxane monomer as in Example 1, can be made soluble in diglyme by reacting in some tolyldiamine as in Example 8.

In general, polyimidesiloxane made with a mixture of, for instance, 2,4- and 2,6-tolyldiamine are more soluble in diglyme than polymers made from a single tolyldiamine such as 1,4-tolyldiamine.

The solubility of the polyimidesiloxanes of the invention in low boiling, non-polar solvents, such as THF, NMP or diglyme is a function of the proportion of the siloxane component in the polyimidesiloxane and is also a function of the siloxane block size. Thus, the siloxane monomer is preferably present in a proportion and has a sufficient block size to render the polyimidesiloxane soluble in a solvent such as THF, NMP or preferably diglyme.

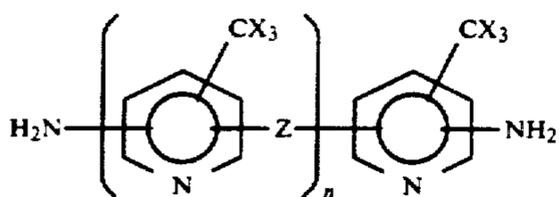
The polyimidesiloxanes of the invention are useful in a variety of applications in the micro-electronic industry. Such applications include use in the form of coatings as interlevel dielectrics and for encapsulation or passivations of semiconductors and hybrid integrated circuits. Coatings of the polyimidesiloxanes can be used in the fabrication of semiconductor devices in the following areas: (a) as a protective overcoat, (b) as an interlayer dielectric for multi-level devices, (c) as an alpha particle barrier, (d) as a non-implant mask, and (e) as an encapsulant. Most of these uses are described in detail by Lee and Craig in Polymer Materials for Electronic Applications, ACS Symposium, Ser. 184, p. 108.

Other uses for the polyimidesiloxanes of the invention include wire and cable coatings, in fibers and films, and molded and extruded articles.

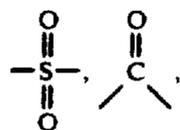
The polyimidesiloxane of BTDA and DATF, such as disclosed in Example 3 is particularly useful for heat sensitive semi-conductors and hybrid integrated circuitry.

I claim:

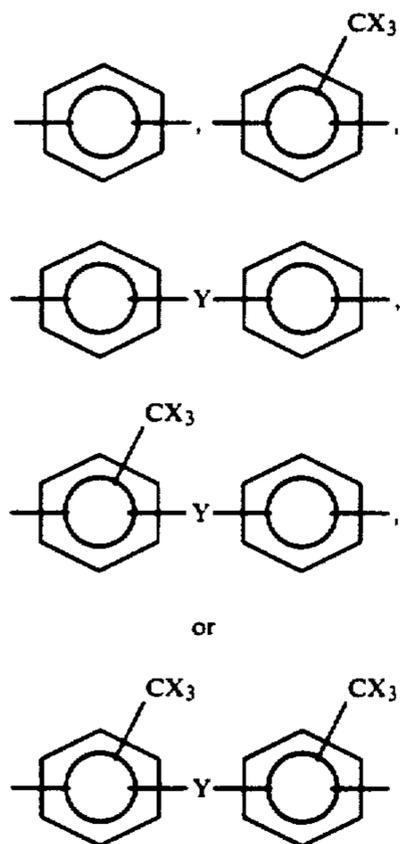
1. In a substantially fully imidized polyimidesiloxane comprising the reaction product of [an] organic dianhydride, [a] difunctional siloxane monomer, and [an] organic [amine] diamine, the improvement wherein the organic [amine] diamine has the formula



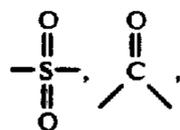
wherein X is hydrogen, halide, phenyl or combinations thereof,



>C(CX<sub>3</sub>)<sub>2</sub>, —, or —Y—Ar—Y—  
Ar =



Y = —O—, —S—,



>C(CX<sub>3</sub>)<sub>2</sub>, or —; and n = 0 or 1.

2. The polyimidesiloxane of claim 1 wherein the organic dianhydride is an oxydiphthalic anhydride.

3. The polyimidesiloxane of claim 1 wherein the organic dianhydride is 4,4'-oxydiphthalic anhydride.

4. The polyimidesiloxane of claim 1 wherein the organic dianhydride is a sulfurdiphthalic anhydride or a sulfone diphthalic anhydride.

5. The polyimidesiloxane of claim 1 wherein the organic dianhydride is 4,4'-sulfurdiphthalic anhydride or 4,4'-sulfone diphthalic anhydride.

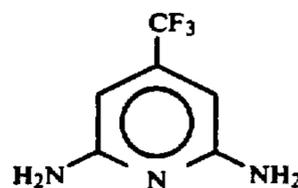
6. The polyimidesiloxane of claim 1 wherein the organic dianhydride is benzophenone tetracarboxylic dianhydride.

7. The polyimidesiloxane of claim 1 wherein the organic dianhydride is biphenyl tetracarboxylic dianhydride.

8. The polyimidesiloxane of claim 1 wherein the organic dianhydride is bis(dicarboxyphenyl)-hexafluoropropene dianhydride.

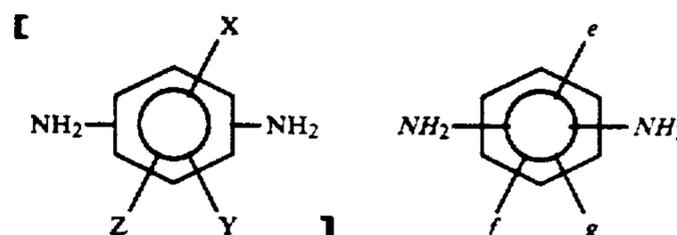
9. The polyimidesiloxane of claim 1 wherein the organic dianhydride is diether dianhydride.

10. The polyimidesiloxane of claim 1 wherein the organic [amine] diamine has the formula



11. The polyimidesiloxane of claim 10 which also comprises an organic diamine which provides an asymmetrical structure in the polyimidesiloxane polymer chain.

12. The polyimidesiloxane of claim 11 wherein [the] an organic diamine [has] having the formula



is included in said reaction product wherein [x, y and z] e, f, and g are independently selected from hydrogen, halogen, alkyl or halogenated alkyl of 1 to 12 carbon atoms or aryl or halogenated aryl of 6 to 12 carbon atoms, provided that all of [x, y and z] e, f, and g are not hydrogen.

13. The polyimidesiloxane of claim 12 wherein [x, y and z] e, f, and g are independently selected from hydrogen, halogen, alkyl of 1 to 12 carbon atoms or aryl of 6 to 12 carbon atoms, provided that all of [x, y and z] e, f, and g are not hydrogen.

14. The polyimidesiloxane of claim 13 wherein the organic diamine is 2,4-tolyldiamine, 2,6-tolyldiamine or a mixture thereof.

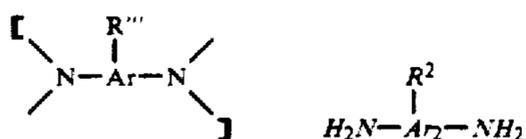
15. The polyimidesiloxane of claim 1 wherein [at least a portion of the] an organic diamine [has] having the formula



is included in said reaction product, wherein [Ar] Ar<sub>2</sub> is an aromatic radical, and R'' is at least one of a hydroxyl, carboxyl, or hydrothiol.

16. The polyimidesiloxane of claim 15 wherein R'' is a carboxyl group or the metal salt of said carboxyl group.

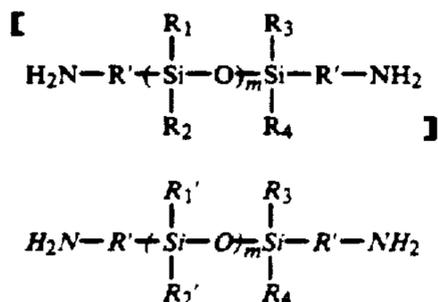
17. The polyimidesiloxane of claim 1 wherein [at least a portion of the] an organic diamine [component has] having the formula



is included in said reaction product wherein [Ar] Ar<sub>2</sub> is an aromatic radical, and [R'''] R<sup>2</sup> is at least one of an arcylic-, an ethylenic- or an acetylenic-bearing radical.

18. The polyimidesiloxane of claim 17 wherein the siloxane monomer is a siloxane diamine.

19. The polyimidesiloxane of claim 18 wherein the siloxane diamine has the formula



wherein each R' is independently selected from the group consisting of substituted [or] aliphatic difunctional radicals of 1 to 12 carbon atoms, unsubstituted aliphatic difunctional radicals of 1 to 12 carbon atoms, [or] substituted [or] aromatic difunctional radicals of 6 to 10 carbon atoms, and unsubstituted aromatic difunctional radicals of 6 to 10 carbon atoms, and wherein [one or more of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can be vinyl, hydroxyl, acrylic-, ethylenic-, or acetylenic-bearing radicals, and the remainder of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>] R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>' and R<sub>4</sub>' are each independently selected from [a] the group consisting of substituted [or] aliphatic monofunctional radicals of 1 to 12 carbon atoms, unsubstituted aliphatic monofunctional [radical] radicals of 1 to 12 carbon atoms, [or] substituted [or] aromatic monofunctional radicals of 6 to 10 carbon atoms, unsubstituted aromatic monofunctional [radical] radicals of 6 to 10 carbon atoms, and hydroxyl, where at least one of R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>' and R<sub>4</sub>' is vinyl, hydroxyl, acrylic-, ethylenic-, or acetylenic-bearing radical, and m is [a number from about 5] 1 to about 200.

20. The polyimidesiloxane according to claim 19 wherein [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are] at least one of R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>', and R<sub>4</sub>' is a methyl [groups] group.

21. The polyimidesiloxane according to claim 20 wherein R' is [-CH<sub>2</sub>-]<sub>3</sub> (-CH<sub>2</sub>)<sub>3</sub>.

22. The polyimidesiloxane of claim 19 wherein at least a portion of the siloxane diamine of the formula comprises a diamine wherein at least one of [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is a radical selected from] R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>', and R<sub>4</sub>' is hydroxyl or vinyl.

23. The polyimidesiloxane according to claim 22 wherein at least one of [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>] R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>', and R<sub>4</sub>' is vinyl and the remainder are methyl groups.

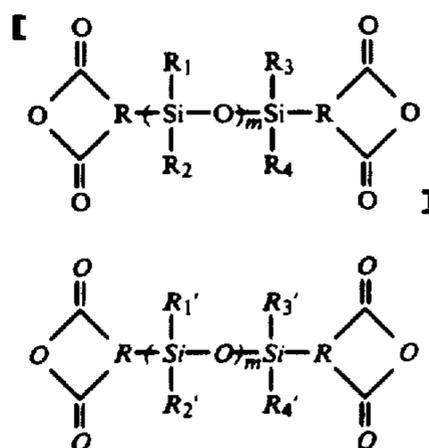
24. The polyimidesiloxane according to claim 23 wherein the R' is (-CH<sub>2</sub>)<sub>3</sub>.

25. The polyimidesiloxane of claim 19 wherein [at least a portion of the siloxane diamine of the formula comprises a siloxane diamine component wherein] at least one of [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is a radical selected from] R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>', and R<sub>4</sub>' is an acrylic-, ethylenic- or acetylenic-bearing [radicals] radical.

26. The polyimidesiloxane of claim 25 comprising an [acrylicbearing] acrylic-bearing radical.

27. The polyimidesiloxane of claim 1 wherein the siloxane monomer is a siloxane dianhydride.

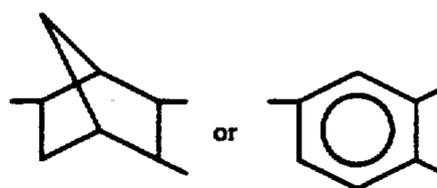
28. The polyimidesiloxane of claim 27 wherein the siloxane dianhydride [as] has the formula



wherein each R is independently selected from the group consisting of substituted [or] aliphatic trifunctional radicals of 1 to 12 carbon atoms, unsubstituted aliphatic trifunctional radicals of 1 to 12 carbon atoms, [or] substituted [or] aromatic trifunctional radicals of 6 to 10 carbon atoms, and unsubstituted aromatic trifunctional radicals of 6 to 10 carbon atoms, and wherein [one or more of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can be halogen, hydride (H), vinyl, hydroxyl, acrylic-, ethylenic-, or acetylenic-bearing radicals, and the remainder of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>, ] R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>', and R<sub>4</sub>' are each independently selected from [a] the group consisting of substituted [or] aliphatic monofunctional radicals of 1 to 12 carbon atoms, unsubstituted aliphatic monofunctional [radical] radicals of 1 to 12 carbon atoms, [or] substituted [or] aromatic monofunctional radicals of 6 to 10 carbon atoms, unsubstituted aromatic monofunctional radicals of 6 to 10 carbon atoms, halogen, hydride (H), and hydroxyl, where at least one of R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>' and R<sub>4</sub>' is halogen, hydride (H), vinyl, hydroxyl, acrylic-, ethylenic-, or acetylenic-bearing radical, and wherein m is [about 5] 1 to about [50] 200.

29. The polyimidesiloxane of claim 28 wherein [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>] R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>', and R<sub>4</sub>' are methyl groups.

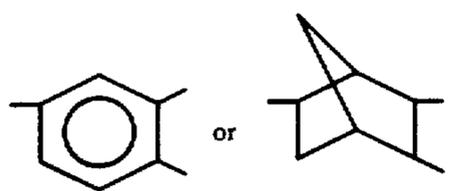
30. The polyimidesiloxane of claim 29 wherein R is



31. The polyimidesiloxane of claim 28 wherein at least a portion of the siloxane dianhydride of the formula comprises a dianhydride wherein at least one of [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>] R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>', and R<sub>4</sub>' is a radical selected from hydride (H), halogen, hydroxyl or vinyl.

32. The polyimidesiloxane according to claim 31 wherein at least one of [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>] R<sub>1</sub>', R<sub>2</sub>', R<sub>3</sub>', and R<sub>4</sub>' is vinyl and the remainder are methyl groups.

33. The polyimidesiloxane according to claim 32 wherein R is



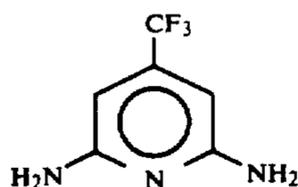
34. The polyimidesiloxane of claim 28 wherein at least a portion of the siloxane dianhydride component of the formula comprises a siloxane dianhydride component wherein at least one of [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>] R<sub>1</sub>' , R<sub>2</sub>' , R<sub>3</sub>' , and R<sub>4</sub>' is a radical selected from acrylic, ethylenic or acetylenic radicals.

35. The polyimidesiloxane of claim 34 comprising an acrylic-bearing radical.

36. A process for producing a polyimidesiloxane that is soluble in diglyme, which comprises reacting a difunctional siloxane monomer, an organic dianhydride and [an amine] a diamine of the formula of claim 1.

37. The process of claim 36 wherein the reaction is conducted in a solvent for the polyimidesiloxane.

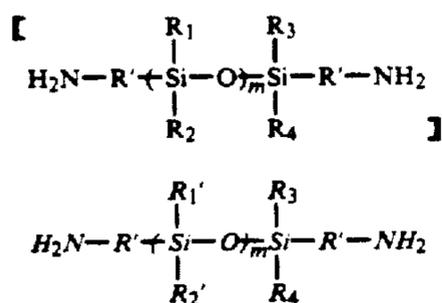
38. The process of claim 37 wherein the [amine] diamine has the formula



and the solvent is selected from diglyme, triglyme, γ-butyrolactone, N,N-dimethylacetamide, 1-methyl-2-pyrrolidinone, tetrahydrofuran, methyl ethyl ketone, phenols or mixtures thereof.

39. The process of claim 36 wherein the siloxane monomer is a siloxane diamine.

40. The process of claim 36 wherein the siloxane monomer is a siloxane diamine having the formula



wherein each R' is independently selected from the group consisting of substituted [or] aliphatic difunctional radicals of 1 to 12 carbon atoms, unsubstituted aliphatic difunctional radicals of 1 to 12 carbon atoms [or] substituted [or] aromatic difunctional radicals of 6 to 10 carbon atoms, and unsubstituted aromatic difunctional radicals of 6 to 10 carbon atoms, and wherein [one or more of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can be vinyl, hydroxyl, acrylic-, ethylenic-, or acetylenic-bearing radicals, and the remainder of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>] R<sub>1</sub>' , R<sub>2</sub>' , R<sub>3</sub>' , and R<sub>4</sub>' are each independently selected from [a] the group consisting of substituted [or] aliphatic monofunctional radicals of 1 to 12 carbon atoms, unsubstituted aliphatic monofunctional [radical] radicals of 1 to 12 carbon atoms [or] substituted [or] aromatic monofunctional radicals of 6 to 10 carbon atoms, unsubstituted aromatic monofunctional radicals of 6 to 10 carbon atoms, and hydroxyl, where at least one of R<sub>1</sub>' , R<sub>2</sub>' , R<sub>3</sub>'

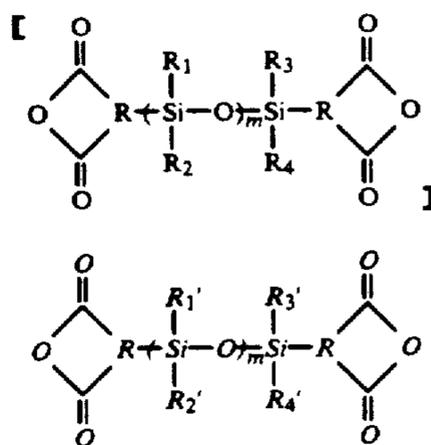
and R<sub>4</sub>' is vinyl, hydroxyl, acrylic-, ethylenic-, or acetylenic-bearing radical, and m is an integer from about [5] 1 to about [50] 200.

41. The process of claim 40 wherein [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>] R<sub>1</sub>' , R<sub>2</sub>' , R<sub>3</sub>' , and R<sub>4</sub>' are methyl groups.

42. The process of claim 41 wherein R' is -(CH<sub>2</sub>)<sub>3</sub>.

43. The process of claim 36 wherein the siloxane monomer is a siloxane dianhydride.

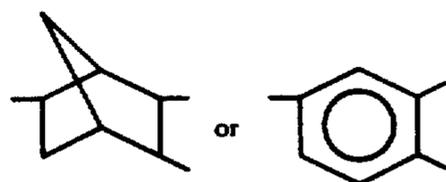
44. The process of claim 43 wherein the siloxane monomer is a siloxane dianhydride having the formula



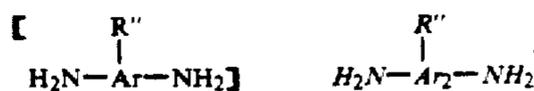
wherein each R is independently selected from the group consisting of substituted [or] aliphatic trifunctional radicals of 1 to 12 carbon atoms, unsubstituted aliphatic trifunctional radicals of 1 to 12 carbon atoms, [or] substituted [or] aromatic trifunctional radicals of 6 to 10 carbon atoms, and unsubstituted aromatic trifunctional radicals of 6 to 10 carbon atoms, and wherein [one or more of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> can be halogen, hydride (H), vinyl, hydroxyl, acrylic-, ethylenic-, or acetylenic-bearing radicals, and the remainder of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>.] R<sub>1</sub>' , R<sub>2</sub>' , R<sub>3</sub>' , and R<sub>4</sub>' are each independently selected from [a] the group consisting of substituted [or] aliphatic monofunctional radicals of 1 to 12 carbon atoms, unsubstituted aliphatic monofunctional [radical] radicals of 1 to 12 carbon atoms [or] substituted [or] aromatic monofunctional radicals of 6 to 10 carbon atoms, unsubstituted aromatic monofunctional radicals of 6 to 10 carbon atoms, halogen, hydride (H), and hydroxyl, where at least one of R<sub>1</sub>' , R<sub>2</sub>' , R<sub>3</sub>' and R<sub>4</sub>' is halogen, hydride (H), vinyl, hydroxyl, acrylic-, ethylenic-, or acetylenic-bearing radical, and wherein m is [about 5] 1 to about [54] 200.

45. The process of claim 44 wherein [R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>] R<sub>1</sub>' , R<sub>2</sub>' , R<sub>3</sub>' , and R<sub>4</sub>' are methyl groups.

46. The process of claim 45 wherein R is



47. The process of claim 36 wherein [at least a portion of the] an organic diamine [has] having the formula



is included in said reaction product, wherein **[Ar]**  $Ar_2$  is an aromatic radical, and  $R''$  is at least one of a hydroxyl, carboxyl, or hydrothiol.

48. The process of claim 47 wherein  $R''$  is **[carboxy]** 5  
carboxyl.

49. The process of claim 40 wherein at least a portion of the siloxane diamine of the formula comprises a diamine wherein at least one of **[R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>]**  $R_1'$ , 10  
 $R_2'$ ,  $R_3'$ , and  $R_4'$  is a radical selected from hydroxyl or vinyl.

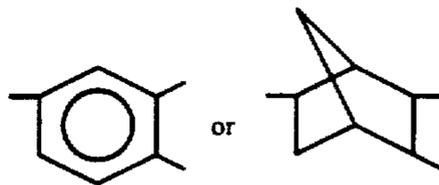
50. The process according to claim 49 wherein at least one of **[R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>]**  $R_1'$ ,  $R_2'$ ,  $R_3'$ , and  $R_4'$  15  
is a vinyl radical, and the remainder are methyl groups.

51. The process according to claim 50 where the  $R'$  is  $-(CH_2)_3-$ .

52. The process of claim 44 wherein at least a portion 20  
of the siloxane dianhydride of the formula comprises a dianhydride wherein at least one of **[R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>]**  $R_1'$ ,  $R_2'$ ,  $R_3'$ , and  $R_4'$  is a radical selected from hydride (H), halogen, hydroxyl, or vinyl. 25

53. The process according to claim 52 wherein at least one of **[R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>]**  $R_1'$ ,  $R_2'$ ,  $R_3'$ , and  $R_4'$  is vinyl and the remainder are methyl groups.

54. The process according to claim 53 wherein R is



55. The process of claim 47 wherein the product of the process is reacted with a compound comprising at least one of an acrylic-, an ethylenic- or an acetylenic-bearing radical.

56. The process of claim 49 wherein the product of the process is reacted with a compound comprising at least one of an acrylic-, an ethylenic- or an acetylenic-bearing radical.

57. The process of claim 52 wherein the product of the process is reacted with a compound comprising at least one of an acrylic-, an ethylenic- or an acetylenic-bearing radical.

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