

NASA CASE NO. *NPO-10767-2*

PRINT FIG. *No Drawing*

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(NASA-Case-NPO-10767-2) HIGHLY FLUORINATED
POLYURETHANES Patent Application E.C.
Stump, Jr., et al (Peninsular ChemResearch,
Inc.) Filed 4 Apr. 1972 12 p CSCI 07C

N72-27151

Unclas

G3/06 33838

NPO

Inventors: Eugene C. Stump, Jr.
Stephen Eugene Rochow

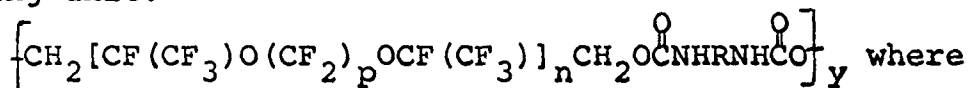
NASA Case NPO-10767-2

Contractor: Peninsular Chemresearch, Inc. October, 1968

HIGHLY FLUORINATED POLYURETHANES

This invention provides new polyurethanes containing a high degree of fluorine atoms. The presence of the fluorine atoms in the polyurethane resins provides material having good thermal stability and chemical resistance.

This invention pertains to polyurethanes having the repeating unit:



n is an integer of 1 to 12,

p is an integer of 2 to 23,

y is an integer of 1 to 1000, and

R is any radical suitable to link isocyanate groups and is preferably selected from the group consisting of alkylene and halogen substituted alkylene radicals of 4 to 12 C atoms, substituted and unsubstituted phenylene groups of up to 20 C atoms.

These polyurethanes are derived from a new hydroxy-terminated perfluoro polyether disclosed in a concurrently filed patent application based upon combined NASA Cases NPO-10765 and 10766. The novel hydroxy terminated material is reacted with a diisocyanate to produce the novel polyurethanes of this invention. The polyurethanes can be used to form seals, coatings, potting material, hoses and the like.

CIP Application Serial No. 241,061
Filed: April 4, 1972

(NPO-10767-2)

Contract NAS7-746

NASA NPO-10767-2

S P E C I F I C A T I O N

TO ALL WHOM IT MAY CONCERN:

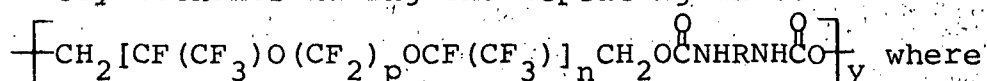
BE IT KNOWN THAT, EUGENE C. STUMP, JR., a citizen of the United States of America, residing at Gainesville, County of Alachua, State of Florida, and STEPHEN EUGENE ROCHOW, a citizen of the United States of America, residing at Ann Arbor, County of Washtenaw, State of Michigan, have invented new and useful

HIGHLY FLUORINATED POLYURETHANES

of which the following is a specification.

ABSTRACT OF THE DISCLOSURE

Polyurethanes having the repeating unit:



n is an integer of 1 to 12,

p is an integer of 2 to 23,

y is an integer of 1 to 1000, and

R is any radical suitable to link isocyanate groups and is preferably selected from the group consisting of alkylene and halogen substituted alkylene radicals of 4 to 12 C atoms, substituted and unsubstituted phenylene groups of up to 20 C atoms.

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 83-568 (72 Stat. 435; 42 USC 2457).

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U. S. application Serial No. 770,417 filed October 24, 1968.

BACKGROUND OF THE INVENTION

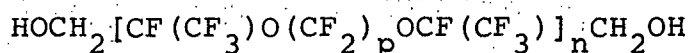
1. Field of the Invention:

The invention is in the field of polymers. More particularly, the invention relates to new highly fluorinated polyurethane polymers.

2. Description of the Prior Art:

Polyurethane resins, also known as isocyanate resins, are a well known class of synthetic polymers. They may be either thermoplastic or thermosetting. The polyurethane resins are made into flexible or rigid foams and flexible and stiff fibers. They are also utilized as coatings, linings, and as elastomers. The polymer units are formed from the reaction of a diisocyanate with a diol. Polyethers have been the most important source of hydroxyl groups. One of the most popular polyethers utilized is polyoxypropylene. Toluene diisocyanate and diphenylmethane-4,4'-diisocyanate are two of the more prevalent diisocyanates reacted to form the polyurethane resins.

In the herein invention, a perfluorinated hydroxy terminated polyether having the general formula



where n is an integer of 1 to 12,

and p is an integer of 2 to 23

is reacted with a diisocyanate to form the polyurethane. In U. S. Patent No. 3,250,807, there is disclosed the basic monomeric ether structure utilized. However, the patent discloses the ether terminated with acid or acid fluoride groupings rather than hydroxyl groupings. In U. S. Patent No. 3,637,842 of January 25, 1972, there is disclosed a method of polymerizing the

1 ethers disclosed in the aforementioned patent such that n is
2 equal to at least 2 to 12. Additionally, the copending appli-
3 cation further discloses converting the acid fluoride terminated
4 polyethers to hydroxy terminated ones. It is these hydroxy
5 terminated perfluoropolyethers that are contemplated as the
6 starting materials utilized herein. Though, as indicated,
7 there are several polyurethane resins available on the
8 commercial market, none would possess the same thermal properties,
9 non-flammability and the like, of polyurethanes using per-
10 fluorinated ethers.

11 OBJECTS OF THE INVENTION

12 An object of this invention is to provide new polyurethane
13 resins having improved oxidative stability.

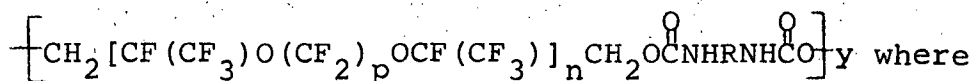
14 Another object of this invention is to provide new
15 polyurethane resins having outstanding chemical resistance and
16 low temperature flexibility.

17 A further object of this invention is to provide highly
18 fluorinated polyurethanes.

19 Other objects will be apparent from the following
20 detailed description and examples.

21 BRIEF SUMMARY OF THE INVENTION

22 This invention relates to new polyurethanes having the
23 formula:



25 n is an integer of 1 to 12,

26 p is an integer of 2 to 23,

27 y is an integer of 1 to 1000, and

28 R is any radical suitable to link isocyanate groups and
29 is preferably selected from the group consisting of
30 alkylene and halogen substituted alkylene radicals of
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1 4 to 12 C atoms, substituted and unsubstituted phenylene
2 groups of up to 20 C atoms.

3 The polyurethane results from the reaction of a diol having the
4 formula $\text{HOCH}_2[\text{CF}(\text{CF}_3)\text{O}(\text{CF}_2)_p\text{OCF}(\text{CF}_3)]_n\text{CH}_2\text{OH}$, where p and n are
5 as defined above, with a suitable diisocyanate such as
6 tetrafluoro-m-phenylene diisocyanate. The formation of the final
7 polyurethane product merely involves heating the two reactants
8 over a wide temperature range for varying lengths of time to
9 obtain products having different properties of hardness, strength
10 and the like. The resultant polyurethanes can be used for
11 films, sheets, seals, and many other applications where good
12 chemical resistance, low temperature flexibility and non-
13 flammability is desired. It is believed the invention will be
14 further understood from the following detailed description and
15 examples.

16 DESCRIPTION OF PREFERRED EMBODIMENTS

17 As indicated, the starting diol prepolymer material
18 utilized to form the polyurethanes of this invention having the
19 general formula

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$$\left[\text{CH}_2[\text{CF}(\text{CF}_3)\text{O}(\text{CF}_2)_p\text{OCF}(\text{CF}_3)]_n\text{CH}_2\text{OCNHRNHC}\overset{\text{O}}{\parallel}\text{O} \right]_y$$
 where

21 n is an integer of 1 to 12,

22 p is an integer of 2 to 23,

23 y is an integer of 1 to 1000, and

24 R is any radical suitable to link isocyanate groups and
25 is preferably selected from the group consisting of
26 alkylene and halogen substituted alkylene radicals of
27 4 to 12 C atoms, substituted and unsubstituted phenylene
28 groups of up to 20 C atoms,

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1 is disclosed in the above-mentioned Patent No. 3,637,842.
2 Briefly, these diols are derived from an acid fluoride terminated
3 corresponding perfluoroether which has first been polymerized
4 and then reduced to change the terminal groups from acid
5 fluoride to hydroxyl. As indicated in the co-pending application,
6 it is preferable that the diols have a molecular weight range
7 of about 1500 to 2000 to provide ease of handling and to produce
8 satisfactory end products.

9 The diisocyanate utilized has the general formula:

10 $\text{OCN}(\text{R})\text{NCO}$ where R is as defined in the above general formula
11 for products of this invention. The halogen substitutions are
12 generally either chlorine or fluorine atoms. The substituted
13 phenylene groups include halogen substitutions, alkyl, aryl
14 and alkaryl groups. To practice this invention, any diisocyanate
15 previously and conventionally utilized to produce polyurethane
16 resins is contemplated. Examples of conventional diisocyanates
17 include toluene diisocyanate, including mixtures of its isomers
18 such as the 2,4 and 2,6 isomer, diphenylmethane-4, 4'-diisocyanate
19 and hexamethylene diisocyanate.

20 Particularly, it is desirable in the herein invention
21 to utilize diisocyanates containing a maximum amount of fluorine
22 atoms. The extremely good chemical resistance, non-flammability
23 and the like can be attributable to the presence of fluorine
24 atoms in the polymer chain. Thus, if the diisocyanate also
25 contains a high substitution of fluorine atoms like the diol
26 utilized, one obtains a polymer containing the desired content
27 of fluorine. Thus, it is preferred to utilize diisocyanates
28 such as tetrafluoro-m-phenylene diisocyanate, tetrafluoro-p-
29 phenylene diisocyanate, and the like.

1 The resultant polymers of this invention will range from
2 sticky semi-solids to tough brittle sheets, depending upon the
3 amount of diisocyanate utilized in the extension and cross
4 linking reaction that transpires between it and the diols. It
5 should be noted that although the hardness of the resultant
6 polymers increases with increasing ratio of diisocyanate to diol,
7 the glass temperature of the resultant polyurethanes is not
8 adversely affected. Thus, it is contemplated to utilize a
9 mole ratio of diisocyanate to diol of from 1:1 up to about 3:1.
10 The preferred mole ratio range of the diisocyanate to diol
11 is between 1:1 and 2:1.

12 The time and temperature of the polymerization reaction
13 is dependent upon the molecular weight of the prepolymer and
14 the type of diisocyanate used. Completion of the polymerization
15 for the given diol and diisocyanate can be determined by the
16 increase in viscosity of the melt polymer. Generally, the
17 temperature of curing can vary from 25° to 100°C, while the
18 time of the cure can range from 10 to 30 minutes.

19 It can be appreciated that the end groups of the polymers
20 of this invention are not readily determined. The polymers can
21 be hydroxy or isocyanate terminations, depending upon the
22 stoichiometry of the reaction, reaction conditions, and the like.
23 Further, since the resultant higher polyurethanes formed are
24 infusible, one cannot determine their molecular weight through
25 available techniques. Thus, a practical upper limit of $y = 1000$
26 is given in the general formula for the products, though the
27 infusible polymers resulting could well have a weight signifi-
28 cantly less than that.

1 As can be seen, the polymers of this invention provide
2 highly fluorinated structures which have many of the good
3 thermal, oxidative, and chemical resistance properties of other
4 known highly fluorinated materials such as Teflon, which is
5 tetrafluorethylene, yet are elastomeric materials and can be
6 utilized as expulsion bladder materials, seals, gaskets,
7 coatings and other similar application.

8 It is believed the invention will be better understood
9 from the following detailed examples:

10 EXAMPLE I.

11 A hydroxy terminated perfluoro polyether having the
12 formula $\text{HOCH}_2[\text{CF}(\text{CF}_3)\text{O}(\text{CF}_2)_5\text{OCF}(\text{CF}_3)]_n\text{CH}_2\text{OH}$ and prepared in
13 accord with the method described in the above mentioned Patent
14 No. 3,637,842 was utilized. This prepolymer had a molecular
15 weight of about 1500. 10.5 grams or .0068 moles of the poly-
16 ether was added together with 2.35 grams or .0101 mole of
17 tetrafluoro-m-phenylene diisocyanate to a 100 ml. resin kettle
18 equipped with a stirrer, N_2 inlet and outlet. The diisocyanate
19 was previously prepared in accord with the procedure set forth
20 by R. Gosnell and J. Hollander in the Journal of Macromolecular
21 Science (Physics) B1(4), 831 (1967). After 20 minutes of
22 stirring at room temperature, the reactants had balled about
23 the stirrer. The material was then removed and placed in a press
24 between 10 mil shims at 3000 psi and 160°C for 1/2 hour. This
25 produced a yellow, flexible sheet of the resultant polymer. The
26 glass transition temperature was -80°C and the Shore A hardness
27 was 79.

28 The above was repeated varying the amounts of prepolymer
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1 and diisocyanates as well as the temperature and time of heating.
2 Hydroxy terminated perfluoropolyether prepolymer of varying
3 molecular weights ranging from 1500 to 2193 was utilized. The
4 results of the various preparations indicating the glass transition
5 temperature T_g and the Shore A hardness, together with an
6 indication as to the type of product, are indicated in the
7 following table:

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TABLE I

Polyurethanes from $\text{HOCH}_2[\text{CF}(\text{CF}_3)\text{O}(\text{CF}_2)_5\text{OCF}(\text{CF}_3)]\text{CH}_2\text{OH}$
and Tetrafluoro-m-phenylene Diisocyanate

| Exp.No. | Prepolymer M.Wt. | Grams Prepolymer | Grams Diisocyanate | Mole Ratio Diisocyanate/ Prepolymer | Temp. °C. | Time (Min.) | Glass Temper- ature Tg(°C) | Hardness ^b | Remarks |
|---------|---------------------|---------------------|-----------------------|---|--------------|----------------|-------------------------------------|-----------------------|--|
| | | | | | | | | | |
| 160.1 | 2193 | 10.63 | 2.24 | 2/1 | 150 | 90 | -73 | - | Brown, flexible film. |
| 160.2 | 2193 | 11.7 | 1.24 | 1/1 | 140 | 180 | - | - | Sticky, semi-solid. |
| 160.3 | 2193 | 10.6 | 3.43 | 3/1 | 140 | 120 | - | - | Weak, elastomeric film. |
| 160.4 | 1500 | 11.35 | 4.17 | 2.38/1 | 50-70 | - | - | - | Brittle, yellow, slightly flexible sheet. |
| 160.5 | 1500 | 9.90 | 1.82 | 1.2/1 | 55-80 | - | - | - | Weak, elastomeric solid. |
| 160.6 | 1500 | 10.1 | 1.56 | 1/1 | 39 | 30 | -5 | 59 | Yellow, elastomeric film, decomposes at 234°. ^a |
| 160.7 | 1500 | 9.05 | 2.10 | 1.5/1 | 25-30 | 10 | - | - | Yellow, elastomeric sheet. |
| 160.8 | 1500 | 11.25 | 2.09 | 1.2/1 | 25-30 | - | -16 | 62 | Yellow, elastomeric film. |
| 160.9 | 1500 | 10.15 | 2.35 | 1.5/1 | 25-30 | 20 | -80 | 79 | Yellow, flexible sheet |
| 160.10 | 1500 | 10.0 | 3.09 | 2/1 | 25-30 | 10 | -79 | 90 | Yellow, slightly flexible sheet. |

a. By Differential Scanning Calorimeter

b. Shore A.

1 Though the materials prepared in the foregoing table
2 were all pressed to form sheets of the polymer of this invention,
3 it should be understood that the material can be formed into
4 various other shapes such as seals, hoses and various forms
5 of coatings.