

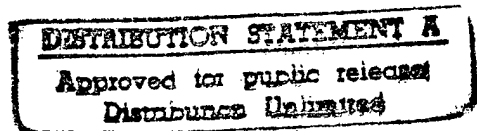
Serial No. 704,029
Filing Date 26 August 1996
Inventor G. W. Lawrence
William H. Gilligan

NOTICE

The above identified patent application is available for licensing. Requests for information should be addressed to:

OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
CODE OCCC3
ARLINGTON VA 22217-5660

DTIC QUALITY INSPECTED 2



19970611 019

2 ENERGETIC FLUORONITRO PREPOLYMER

3 BACKGROUND OF THE INVENTION

4 This invention relates to polymers and more particularly
5 to energetic polymers which are useful as binders in
6 propellants and explosives.

7 At the present time non-energetic binders are used for
8 propellants and explosives. Energetic plasticizers are
9 frequently combined with these binders to increase the energy.
10 Unfortunately, the amounts of energetic plasticizer needed
11 result in reductions in important properties such as tensile
12 strength and elongation.

13 It would be desirable therefore to reduce the amounts of
14 energetic plasticizers needed in explosive and propellant
15 binders and thus improve physical properties such as tensile
16 strength and elongation.

17 SUMMARY OF THE INVENTION

18 Accordingly, an object of this invention is to provide
19 new polymers.

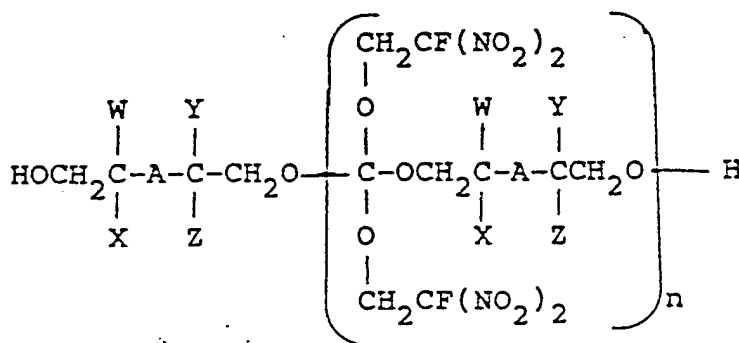
20 Another object of this invention is to provide new high
21 energy polymers.

22 A further object of this invention is to provide polymers
23 having a high concentration of stable, high energy
24 2-fluoro-2,2-dinitroethyl groups.
25
26
27

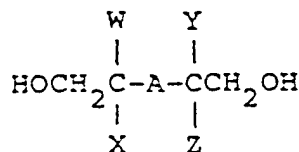
1 Yet another object of this invention is to provide means
 2 of increasing the energy content of binders without
 3 sacrificing tensile strength and elongation.

4 A still further object of this invention is to provide a
 5 new method of synthesizing energetic polymers.

6 These and other objects of this invention are achieved by
 7 providing hydroxy-terminated poly(2-fluoro-2,2-dinitroethyl)
 8 polynitroorthocarbonates prepolymers of the formula



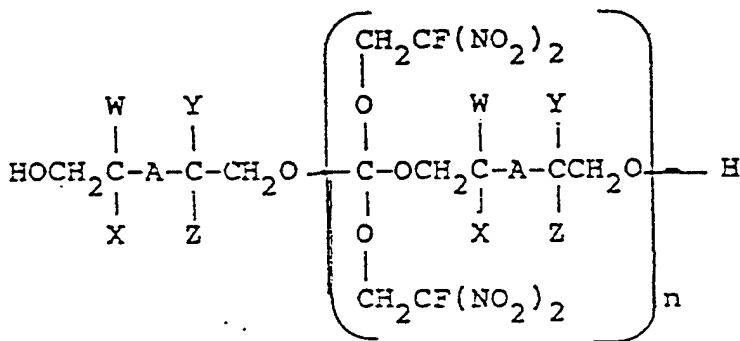
15
 16 wherein W, X, Y, and Z vary independently and are F or NO₂,
 17 and -A- is -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, -CF₂-, -CF₂CF₂-,
 18 -CF₂CF₂CF₂-, -CF₂CF₂CF₂CF₂-, -CH₂OCH₂-, -CH₂OCH₂OCH₂-,
 19 -CH₂OCF₂OCH₂-, or -CH₂N(NO₂)CH₂-. These compounds are
 20 prepared by reacting bis(2-fluoro-2,2-
 21 dinitroethyl)dichloroformal with a diol of the formula



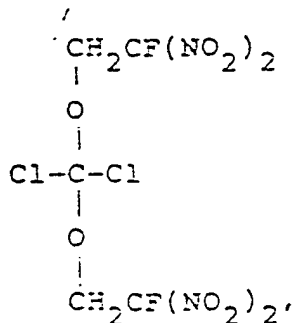
1 wherein W, X, Y, Z, and -A- are as defined above. These
 2 prepolymers react with polyisocyanates (functionality 2.0 -
 3 3.0) to form energetic, rubbery polymeric binders.

4
 5 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

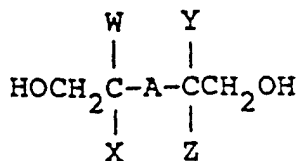
6 The prepolymers of this invention are energetic hydroxy-
 7 terminated poly(2-fluoro-2,2-dinitroethyl)
 8 polynitroorthocarbonates prepolymers of the general formula



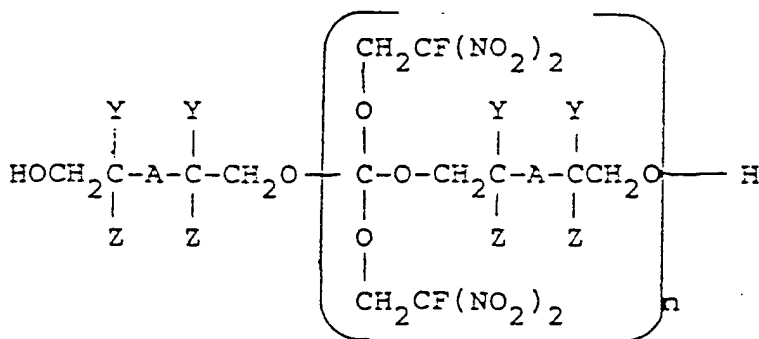
16 which are prepared by reacting bis(2-fluoro-2,2-
 17 dinitroethyl)dichloroformal,



24 with a diol of the general formula
 25
 26
 27

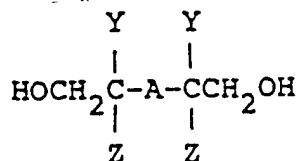


1
 2
 3
 4 where W, X, Y, and Z vary independently and are each F or NO₂,
 5 and A represents a stable, nonreactive, preferably energetic
 6 linkage which will be described later. It is critical for the
 7 formation of stable poly(2-fluoro-2,2-dinitroethyl)
 8 polynitroorthocarbonates that W, X, Y, and Z each be a very
 9 strong electronegative fluoro or nitro group. In other words,
 10 the carbon atoms beta to the terminal hydroxy groups must each
 11 contain two of these strongly electronegative groups. Thus,
 12 the diols used in this invention will contain only -CF₂CH₂OH-,
 13 -CF(NO₂)CH₂OH-, and -C(NO₂)₂CH₂OH- end groups. Preferably the
 14 two end groups on the diol will be identical (W equal to Y and
 15 X equal to Z). The general formula for these preferred
 16 polyfluorodinitroethyl polynitroorthocarbonates is



17
 18
 19
 20
 21
 22
 23
 24 and the general formula for the corresponding diol starting
 25 material is

26
 27



wherein Y and Z vary independently and are each F or NO₂.

As stated before, -A- may represent any one of a number of linkages provided that it is stable and is nonreactive under the conditions of the polymerization process. For example -A- may contain -CH₂-, -CHF-, -CF₂-, -CH(NO₂)- and -C(NO₂)₂- units. -A- may also contain oxygen in the form of ether (e.g., -CH₂OCH₂-, -CF₂OCF₂-, etc.) or formals (e.g., -CH₂OCH₂OCH₂-, -CH₂OCF₂OCH₂-, etc.) units. However, unstable oxygen groups such as peroxides (-CH₂-O-O-CH₂-) are excluded. Oxygen in a reactive form such as -CH(OH)- is also excluded from -A-. Additionally, nitrogen may be present in the backbone of -A-. However, -NH-contains a reactive hydrogen and therefore is not desirable; on the other hand, -N(NO₂)-is stable, energetic, and nonreactive and therefore suitable.

Preferably, -A- can be -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, -CF₂ -, -CF₂CF₂-, -CF₂CF₂CF₂-, -CF₂CF₂CF₂CF₂-, -CH₂OCH₂-, -CH₂OCH₂OCH₂ -, -CH₂OCF₂OCH₂-, or -CH₂N(NO₂)CH₂-.

The following are examples of the diols which may be reacted with bis(2-fluoro-2,2-dinitroethyl)dichloroformal to form the hydroxy-terminated polyfluorodinitroethyl polynitroorthocarbonate prepolymers of this invention:

- 1 $\text{HOCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH},$
- 2 $\text{HOCH}_2\text{CF}(\text{NO}_2)\text{CH}_2\text{OCH}_2\text{OCH}_2\text{CF}(\text{NO}_2)\text{CH}_2\text{OH},$
- 3 $\text{HOCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OCF}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH},$
- 4 $\text{HOCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH},$
- 5 $\text{HOCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH},$
- 6 $\text{HOCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{NO}_2)_2\text{CH}_2\text{OH},$
- 7 $\text{HOCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH}$
- 8 $\text{HOCH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH},$
- 9 $\text{HOCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OH},$ and
- 10 $\text{HOCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}.$

11 Note that long hydrocarbon chains, $-(\text{CH}_2)_n-$, are undesirable
12 because they substantially reduce the energy content of the
13 polymer. On the other hand, polyfluorohydrocarbon and
14 polynitrohydrocarbon chains are preferred because of their
15 energy content.

16 Note that the -A- linkage in the diols is preferably a
17 straight chain as this will produce a more flexible
18 propellant binder.

19 Equimolar amounts of the diol and
20 bis(2-fluoro-2,2-difluoroethyl)dichloroformal can be used, but
21 preferably an excess of the diol is used to assure that the
22 prepolymer product will be hydroxy-terminated. The molar
23 ratio of diol to bis(2-fluoro-2,2-dinitroethyl)dichloroformal
24 is from 1:1 to 2:1 and preferably from 1.33:1 to 1.50:1.

25
26
27

1 Preferably the average molecular weight of the hydroxy-
2 terminated poly(2-fluoro-2,2-dinitroethyl)
3 polynitroorthocarbonate prepolymer is from 1,000 to 10,000.
4 As the molar ratio of diol to bis(2-fluoro-2,2-
5 dinitroethyl)dichloroformal is increased, the average
6 molecular weight of the prepolymer produced decreases.

7 The polymerization reaction between a diol and the
8 bis(2-fluoro-2,2-dinitroethyl)dichloroformal can be run
9 without a solvent by melting the starting materials. However,
10 it is safer and thus preferable to use a solvent. Preferred
11 among the solvents are the chlorohydrocarbons such as
12 methylene chloride; 1,2-dichloroethane, 1,1,1-trichloroethane,
13 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, and
14 chloroform, with chloroform being the preferred solvent.
15 Nitromethane can also be used as the solvent.

16 The reaction temperature is preferably from about 50°C to
17 about 100°C and more preferably from 60°C to 65°C.

18 Preferably a rapid stream of nitrogen is passed through
19 the reaction mixture to remove hydrogen chloride which is
20 generated by the reaction between the diol and
21 bis(2-fluoro-2,2-dinitroethyl)dichloroformal. It is
22 advantageous to collect and titrate the evolved hydrogen
23 chloride to determine and confirm the extent of reaction.

24 Crude poly(2-fluoro-2,2-dinitroethyl)polynitroortho-
25 carbonate material is obtained either by solvent evaporation
26 or by decantation of the supernatant liquid from the cooled
27

1 reaction mixture. Purified material is obtained by extracting
2 the low molecular weight impurities from the crude material
3 with suitable solvents and/or solvent combinations. For
4 example, a chloroform or a mixture of a few percent (~2%) of
5 methanol in chloroform will work.

6 The purified hydroxy-terminated poly(2-fluoro-2,2-
7 dinitroethyl) polynitroorthocarbonate prepolymers can be
8 reacted with suitable materials to produce energetic, plastic
9 binders from explosives and propellants. For example, as
10 illustrated by Examples 4 and 6, these prepolymers may be
11 cured with polyisocyanates to produce rubbery polymers.

12 Organic polyisocyanate which may be used in this invention
13 include aromatic, aliphatic and cycloaliphatic diisocyanates,
14 as for example: 2,4-toluene diisocyanate, 2,6-toluene
15 diisocyanate, p-phenylene diisocyanate, 1,5-naphthylene
16 diisocyanate, 4,4'-biphenylene diisocyanate, p,p'-methylene
17 diphenyl diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-
18 hexamethylene diisocyanate, 1.10-decamethylene diisocyanate,
19 1,4-cyclohexylene diisocyanate, 4,4'-methylene-bis-cyclohexyl
20 isocyanate), 1,5-tetrahydronaphthylene diisocyanate, and
21 polymethylenepolyphenylisocyanate (PAPI), isophorone
22 diisocyanate, and N,N',N''-trisisocyanatohexylbiuret. Mixture of
23 diisocyanates may also be used. Preferred polyisocyanates are
24 2,4-toluene diisocyanate, polymethylpolyphenylisocyanate
25 (PAPI), and N,N',N''-trisisocyanatohexylbiuret. The
26 polyisocyanate is used in an amount sufficient to supply from
27

1 about 0.8:1 to about 1.5:1 but preferably from 1:1 to 1.2:1
2 isocyanate functional groups for each hydroxy functional
3 group.

4 The general nature of the invention having been set
5 forth, the following examples are presented as specific
6 illustrations thereof. It will be understood that the
7 invention is not limited to these examples but is susceptible
8 to various modifications that will be recognized by one of
9 ordinary skill in the art.

11 Examples

12 Examples 1 and 2 illustrate methods by which the
13 bis(2-fluoro-2,2-dinitroethyl)dichloroformal starting material
14 can be prepared. These examples are taken from U.S. Patent
15 Application Serial No. 256,462 which was filed on March 30,
16 1981, by William H. Gilligan and which now is under a D-10
17 order.

18 Example 1

19 Bis(2-fluoro-2,2-dinitroethyl)dichloroformal

20 To a solution of 10.0g (28.6 mmol) of bis(2-fluoro-2,2-
21 dinitroethyl) thionocarbonate in 50 ml of freshly distilled
22 sulfuryl chloride was added 4.0 ml of titanium tetrachloride.
23 The solution was then refluxed for 5 days. Excess sulfuryl
24 chloride and titanium tetrachloride were then removed in vacuo
25 at a bath temperature of 50°C. The solid residue was

26
27

1 recrystallized from chloroform to give 7.91g (71%) of
2 bis(2-fluoro-2,2-dinitroethyl)dichloroformal as colorless
3 crystals, mp 57-58°C.

4 H - NMR (CDCl₃/TMS) δ (ppm) - d, 5.02.

5 Calc. for C₅H₄Cl₂F₂N₄O₁₀: C, 15.44; H, 1.04;

6 Cl, 18.23; F, 9.77; N, 14.40

7 Found: C, 15.46; H, 1.05; Cl, 18.40; F, 9.98; N, 14.11.

8
9 Example 2

10 Bis(2-fluoro-2,2-dinitroethyl)dichloroformal

11 Gaseous chlorine was slowly passed into a stirred slurry
12 of 21.0g (0.067 mol) of bis(2-fluoro-2,2-
13 dinitroethyl)thionocarbonate in 100 ml of dry carbon
14 tetrachloride and 10 ml of dry trifluoroethanol for 4.5 hours
15 at the end of this period the slurry had changed into a clear
16 orange-colored solution. After standing overnight, volatiles
17 were removed on a rotovac and the solid residue was
18 recrystallized from chloroform to give 19.33 g (83%) of
19 bis(2-fluoro-2,2-dinitroethyl)dichloroformal, m.p. 57-8°C.

20 The bis(2-fluoro-2,2-dinitroethyl)thiocarbonate used in
21 examples 1 and 2 can be prepared according to the method
22 disclosed in example 1 of U.S. Patent No. 4,172,088, entitled
23 "Bis(2-Fluoro-2,2-dinitroethyl)thionocarbonate and a method of
24 Preparation," which issued on October 23, 1979, to Angres et
25 al.

Example 3

1
2 To a three-necked, round bottomed flask equipped with a
3 nitrogen inlet, a motor driven stirrer, and an insulated
4 spiral condenser outlet which was cooled at -30°C were added
5 2,2,8,8-tetranitro-4,6-dioxanonane-1,9-diol (DINOL, 20.0 g,
6 0.0581 mol), bis(2-fluoro-2,2-dinitroethyl)dichloroformal
7 (19.31 g, 0.0496 mol) and 1,2-dichloroethane (13.0 mL). A
8 preheated 75°C oil bath was raised around the flask causing
9 the contents to form a solution quickly. A rapid, steady
10 stream of nitrogen was passed through the solution via a
11 sintered glass sparge tube throughout the course of the
12 reaction. After six days, 98.24% of the calculated amount of
13 hydrogen chloride had been trapped by an aqueous sodium
14 hydroxide solution (0.1 N). A white solid was isolated by
15 evaporation of the solvent under vacuum and allowing the foam
16 thus formed to solidify. The hydroxyl equivalent weight
17 corrected for the extent of reaction was 1785, measured from
18 the decrease in the infrared absorption of
19 toluenesulfonylisocyanate. The number average molecular
20 weight calculated from the reactant ratio corrected for the
21 extent of reaction was 3792. Thus, the functionality was
22 2.12.

Example 4

23
24 The prepolymer produced in example 3 (4.00 g) dissolved
25 in bis(2-fluoro-2,2-dinitroethyl)formal (FEFO, 4.84 g) was
26
27

1 degassed under vacuum overnight at 60°C. Isophorone
2 diisocyanate (0.17 g), N,N',N''-trisisocyanatohexylbiuret (0.13
3 g), and dibutyltin dilaurate (0.004 g) were added. The
4 solution was degassed under vacuum for 20 minutes and cured at
5 60°C for four days to form a clear elastic gumstock.

6
7 Example 5

8 2,2,8,8-tetranitro-4,6-dioxanonane-1,9-diol (60.0 g,
9 0.174 mol), bis(2-fluoro-2,2-dinitroethyl)dichloroformal
10 (54.25 g, 0.139 mol), and ethanol-free chloroform (51.0 mL)
11 were added to a three-necked, round bottomed flask equipped
12 with a nitrogen sparge tube inlet, an insulated, spiral
13 condenser outlet at -25°C, and a motor driven stirrer. A
14 preheated 60-65°C oil bath was raised around the flask causing
15 the contents to form a solution quickly. A rapid, steady
16 stream of nitrogen was passed through the solution throughout
17 the course of the reaction. After 25 hours, 81% of the
18 calculated amount of hydrogen chloride had been trapped in an
19 aqueous sodium hydroxide (0.1 N) solution. The supernatant
20 liquid was decanted from the cooled mixture. The residue in
21 the flask was extracted with stirring two times with 2%
22 methanol-chloroform and two times with 100% chloroform. The
23 remaining solvent was removed in vacuo, and the solid foam was
24 powdered.

1 Yield: 69.85 g (66.93% overall yield, 95.92% based on the
2 extent of reaction). The hydroxyl equivalent weight of the
3 material, corrected for the presence of some (~5-8%)
4 nonfunctional cyclic orthocarbonate, was 998.3 g/eq. OH.
5 Analysis by gel permeation chromatography gave the following
6 corrected values: weight average molecular weight of 2830,
7 number average molecular weight of 2121, and dispersity of
8 1.33. Thus, the average functionality of the chains above
9 1000 molecular weight is 2.12.

11 Example 6

12 The prepolymer prepared in example 5 (4.00 g) and
13 dibutyltin dilaurate (0.04 g), dissolved in
14 bis(2-fluoro-2,2-dinitroethyl)formal (5.55 g) were degassed
15 under vacuum for two hours at 55°C. Toluene diisocyanate
16 (0.27 g) and an aromatic polyfunctional isocyanate (trade
17 name: PAPI 135, Upjohn Co., 0.095 g) were added. The solution
18 was degassed under vacuum at 55°C for four hours and cured at
19 ambient pressure at 55°C for seven days with a few bubbles
20 showing up after two days to form an elastic gumstock.

Example 7

DEGREE OF REACTION UNDER DIFFERENT CONDITIONS

REACTION CONDITIONS				RESULTS
<u>Run</u>	<u>Solvent*</u>	<u>Temperature</u>	<u>Time (hrs.)</u>	
1.	No solvent	80-85°C	24	crosslinked material
2.	20% FEFO**	80°C	25	crosslinked material
3.	30% to 50% FEFO	75°C	48	incomplete reaction
4.	29% CH ₂ ClCH ₂ Cl	75°C	144	complete reaction
5.	26% CH ₃ NO ₂	75°C	60	complete reaction
6.	26% CH ₃ NO ₂	85°C	36	complete reaction
7.	1,2-dimethoxy- ethane, gamma- butyrolactone BF ₃ ·Et ₂ O			incomplete reaction
8.	26% CH ₃ NO ₂	70°C	72	94% complete reaction
9.	26% CHCl ₂ CHCl ₂	70°C	72	95% complete reaction
10.	26% CHCl ₂ CHCl ₂ + Dinol	70°C	39	complete reaction
11.	24% CHCl ₃	65°C	24	67% complete reaction

*Weight percentage of solvent based on the total weight of the solvent plus reactants

** FEFO is bis(2-fluoro-2,2-dinitroethyl)formal.

Example 8

Properties of Bis(2-fluoro-2,2-dinitroethyl)dichloroformal/dinol
prepolymer

Appearance: White Powder

Melting Range: 60-100°C

Vacuum Thermal Stability (120°C, 48 H): 1.01 cc/g

Density: 1.67 g/mL

Heat of Formation: -603.8 cal/g

Calculated Detonation Pressure (Kamlet-Jacobs): 258 Kbar

Electrostatic Sensivity: >12.5 joules

Sliding Friction: >980 ft-lbs

Obviously, many modifications and variations of the
present invention are possible in light of the above
teachings. It is therefore to be understood that
the invention may be practiced
otherwise than as specifically described.

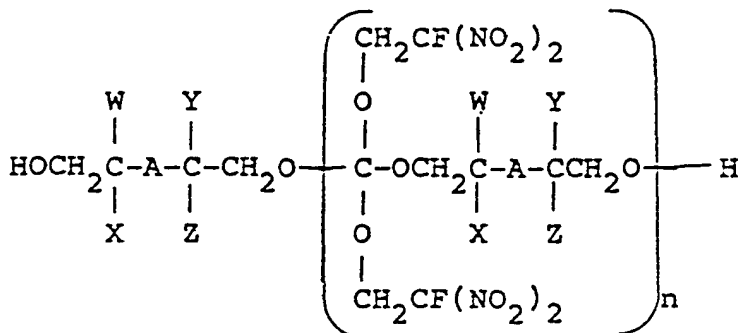
77915

Navy Case No. 68,377

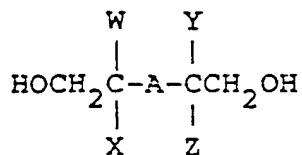
ENERGETIC FLUORONITRO PREPOLYMER

ABSTRACT

Hydroxy-terminated poly(2-fluoro-2,2-dinitroethyl) polynitroorthocarbonate prepolymers of the formula



which are prepared by reacting bis(2-fluoro-2,2-dinitroethyl)dichloroformal with a diol of the formula



wherein W, X, Y, and Z vary independently and are F or NO₂, and wherein A is -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, -CF₂-, -CF₂CF₂-, -CF₂CF₂CF₂-, -CF₂CF₂CF₂CF₂-, -CH₂OCH₂-, -CH₂OCH₂OCH₂-, -CH₂OCF₂OCH₂-, or -CH₂N(NO₂)CH₂-. These prepolymers are reacted with curing agents (e.g., polyisocyanates) to form energetic polymeric binders.