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3,245,962

N-NITRO SUBSTITUTED, NITRO CONTAINING POLYURETHANES

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20 Claims. (Cl. 260—77.5)

This invention relates to high molecular weight polyurethane polymers containing nitro groups.

This application is a continuation-in-part of applicant's copending U.S. application, Serial No. 87,710, filed February 7, 1961, now U.S. Patent 3,087,061.

The principal object of this invention is to prepare high energy high molecular weight compounds useful as solid smokeless propellants.

The nitro-substituted polyurethanes of my invention are high energy solid propellants and can be used as a primary propulsion source in rocket propelled vehicles and can also be used as a propellant for artillery missiles. When used as the primary propulsion source for rocket vehicles, they can be conveniently ignited by a conventional igniter such as, for example, the igniter disclosed in assignee's copending United States patent application, Serial No. 306,030, filed August 23, 1952, now U.S. Patent No. 3,000,312. The propellant is preferably cast in place in tubular form and restricted in the conventional manner with a relatively inert resin such as a nonnitrated polyurethane foam or a polyester resin inside a chamber having one end open and leading into a conventional venturi rocket nozzle. Upon ignition, large quantities of gases are produced and exhausted through the nozzle, creating propulsive force.

The polyurethanes of my invention possess numerous advantages over the composite and double-base solid propellants commonly in use today. In the propellant substances of my invention, the oxidizer is an integrated part of the chemical compound, thereby enhancing the reproducibility of ballistic properties and eliminating dangerous and costly grinding and mixing operations. In propellant compositions commonly in use at present, the oxidizing element is usually a finely divided inorganic oxidizing salt which is dispersed in some type of combustible organic binder, usually an organic resin. Numerous problems are involved in the preparation of this type of propellant; namely, obtaining uniform dispersion of the oxidizing agent throughout the binding composition and at the same time preventing the formation of cracks and faults in the propellant grain itself.

Although it is desirable to avoid the need for incorporating additional oxidizer, additional oxidizer can, if desired, be added to the novel resins of my invention.

Any solid inorganic oxidizing salt such as ammonium perchlorate, ammonium nitrate, or the like, can be used for this purpose in a conventional manner. For example, the method disclosed in assignee's U.S. patent application, Serial No. 829,180, filed July 20, 1959, can be used by merely substituting the high energy resins of this invention for the fuel binder materials disclosed therein.

The polyurethanes of my invention, having no metals whatsoever present, are smokeless and, since all the elements of the propellant are integrated in the molecular chain itself, there are no difficulties encountered in dispersing the oxidizing component nor is it necessary to perform any difficult and dangerous grinding and mixing operations.

The high specific impulse and high density of the polyurethane compositions of my invention render them extremely valuable wherever weight and size considerations of the propellant charge are important.

In addition to these valuable propellant properties, it has also been found that my materials possess high temperature and impact stability, thereby rendering their production both safe and economical.

The polyurethanes of my invention are conveniently prepared by post-nitrating the polyurethanes disclosed in applicant's copending U.S. application, Serial No. 87,710, filed February 7, 1961. In this manner, additional nitro groups are incorporated into the polyurethanes disclosed in application, Serial No. 87,710, thereby creating a product with a higher nitro content and thus higher energy.

The polyurethanes to be post-nitrated are conveniently prepared by reacting a diisocyanate with a diol, in accordance with the general reaction scheme set forth in U.S. patent application, Serial No. 87,710 shown below:

$$y(HO{-}R'{-}OH) + y(OCN{-}R{-}NCO) \longrightarrow [{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R'{-}O{-}]_y$$

wherein R is a lower alkylene, nitroalkylene, nitrazaalkylene, or nitrazanitroalkylene radical; R′ is a lower alkylene, nitroalkylene, nitrazaalkylene, nitrazanitroalkylene, dialkoxynitroalkylene, or dialkyloxamide radical and y is a whole number greater than one, the number of repeating units in the polymer chain. It will be appreciated that in any given batch of propellant, individual molecules may vary in length from several to tens of thousands of repeating units, hence, molecular weight figures represent statistical averages. The exact nature of terminal groupings is not known and will vary depending upon whether plasticizers, polymerization agents, etc. are present. Moreover, a given molecule may even form a ring and thus leave no dangling radicals.

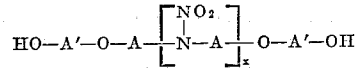
It has been found that the reaction time may be shortened and higher molecular weight polymers obtained, for example, polyurethanes having molecular weights of the order of about 75,000, by conducting the reaction in solution in the presence of a suitable catalyst. Any of the conventional catalysts used in the preparation of polyurethane resins can be used; however, several catalysts have been found particularly useful, among which are boron trichloride; boron trifluoride complexes, such as boron trifluoride etherate; and metal chelates, such as ferric acetylacetonate. Suitable solvents are 1,4-dioxan, N,N-dimethylformamide, butyrolacetone, acetone, etc. where catalysts are employed, they can be used in quantities within the range from mere traces up to amounts equivalent to about 1 percent by weight of the total mass or even higher. The use of catalysts is not critical; however, for economic reasons it is usually preferable to use them.

The polyurethane starting compounds can comprise either linear polymers or cross-linked polymers. The linear polymers are those formed from appropriate isocyanates and alcohols without the addition of any cross-linking agent. That is, they are merely linear chains composed of alternate isocyanate and alcohol monomers. The cross-linked polymers, on the other hand, are prepared by employing a cross-linking agent in addition to the isocyanate and alcohol monomers which acts as a bridge between the linear isocyanate-alcohol polymers, thus bonding these polymers together. Any suitable cross-linking agent such as polyisocyanates, triols, glycerol, trimethylol-propane, tris-(hydroxymethyl)nitromethane, etc., can be used.

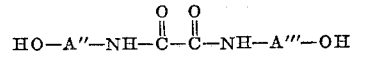
The polyurethane polymerization reaction can be effectively carried out at any temperature, the only effect of temperature variation being a corresponding change in the rate of reaction. The polymerization can be conducted at room temperature although higher temperatures increase the rate of reaction and might be de-

sirable in certain cases. However, the polymerization will also take place at temperatures much below room temperature and thus temperature is not a critical variable.

It is evident from the reaction scheme set forth above that a wide variety of polyurethane starting compounds can be prepared simply by varying the particular alcohol and isocyanate used in the reaction. Examples of diols which may be used are dialkoxynitrazaalkylene diols having the general formula:



wherein A and A' are the same or different and are lower alkylene radicals and x is a whole number from 1 to 6, inclusive, and dihydroxyalkyloxamides having the general formula



wherein A'' and A''' are the same or different and are lower alkylene radicals. Specific examples of diols are:

N,N'-bis(2-hydroxyethyl)oxamide;
N,N'-bis(3-hydroxypropyl)oxamide;
N,N'-bis(-hydroxymethyl)oxamide;
N,N'-bis(6-hydroxyhexyl)oxamide;
N,N'-bis(2-hydroxypropyl)oxamide;
N(2-hydroxyethyl)N'-(3-hydroxypropyl)oxamide;
2,2-dinitro-1,3-propanediol;
1,3-propanediol;
2-nitro-2-ethyl-1,3-propanediol;
3,3-dinitro-1,5-pentanediol;
2,2,4,4-tetranitro-1,5-pentanediol;
5,5,5-trinitro-1,2-pentanediol;
2-nitro-2-methyl-1,3-propanediol;
4,4,6,8,8-pentanitro-1,11-undecanediol;
4,4,6,6,8,8-hexanitro-1,11-undecanediol;
Ethylene glycol;
5,5-dinitro-1,2-hexanediol;
3-nitraza-1,5-pentanediol;
2-nitro-2-bromo-1,3-propanediol;
1,4-butanediol;
2-nitro-2-chloro-1,3-propanediol;
3,6-dinitraza-1,8-octanediol;
2-butyne-1,4-diol;
5-nitro-5-aza-3,7-dioxa-1,9-nonanediol;
5,7-dinitro-5,7-diaza-3,9-dioxa-1,11-undecanediol;
5,7,9-trinitro-5,7,9-triaza-3,11-dioxa-1,13-tridecanediol;
5,7,9,11-tetranitro-5,7,9,11-tetraza-3,13-dioxa-1,15-pentadecanediol;
5,7,9,11,13-pentanitro-5,7,9,11,13-pentaza-3,12-dioxa-1,17-heptadecanediol;
6-nitro-6-aza-4,8-dioxa-1,11-undecanediol;
6,8-dinitro-6,8-diaza-4,10-dioxa-1,13-tridecanediol;
6-nitro-6-aza-3,9-dioxa-1,11-undecanediol;
6,8-dinitro-6,8-diaza-3,11-dioxa-1,13-tridecanediol;
7-nitro-7-aza-4,10-dioxa-1,13-tridecanediol;
9-nitro-9-aza-7,11-dioxa-1,17-heptadecanediol;
5,9-dinitro-5,9-diaza-3,11-dioxa-1,13-tridecanediol;
6,12-dinitro-6,12-diaza-3,15-dioxa-1,17-heptadecanediol; and
5,7,9,11,13-pentanitro-5,7,9,11,13-pentaza-3,16-dioxa-1,18-octadecanediol.

Examples of isocyanates which may be used are:

Lower alkylene diisocyanates such as—
Methylene diisocyanate,
Ethylene diisocyanate, and
1,3-propane diisocyanate,
Hexamethylene diisocyanate;

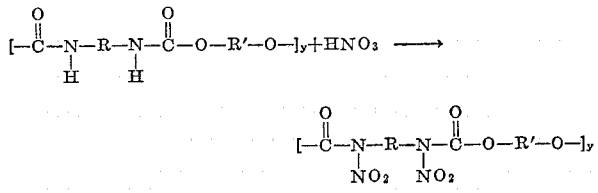
Nitroalkylene diisocyanates such as—
3,3-dinitro-1,5-pentane diisocyanate
3,3,5,7,7-pentanitro-1,9-nonane diisocyanate,
2,2,4,4-tetranitro-1,5-pentane diisocyanate, and
5,5,5-trinitro-1,2-pentane diisocyanate;

Nitrazaalkylene diisocyanates such as—
2,5-dinitraza-1,6-hexane diisocyanate,
3,6-dinitraza-1,8-octane diisocyanate,
3-nitraza-1,5-pentane diisocyanate, and
2-nitraza-1,4-pentane diisocyanate; and

Nitrazanitroalkylene diisocyanates such as—
5-aza-3,3,5,7,7-pentanitro-1,9-nonane diisocyanate,
6-aza-3,6-dinitro-1,8-octane diisocyanate; and
5-aza-3,3,5-trinitro-1,9-nonane diisocyanate.

Any of the above-named alcohols and isocyanates and mixtures thereof can be polymerized to form starting compounds of this invention.

The post-nitration procedure of this invention proceeds in accordance with the following general reaction scheme:



wherein y, R and R' have the meaning previously set forth in the specification.

Two procedures may be used to accomplish the post-nitration as follows:

Procedure A.—The polyurethane polymer starting compound is dissolved in an excess of 100 percent nitric acid at a temperature of about —40° C. to about 65° C. 0° C. is prefered since it is easiest to maintain. The solution is immediately precipitated by pouring the acid solution into cold water, preferably ice-water. The post-nitrated polyurethanes of the invention may then be washed free of acid with any suitable washing agent such as water, recovered by any of the common liquid-solid separation means, such as filtration, decantation or centrifugation, and then dried.

Procedure B.—The polyurethane polymer starting compound is dissolved in an excess of 100 percent nitric acid at about —40° C. to about 65° C. 0° C. is preferred since it is easiest to maintain. The acid is then removed by distillation and the residue is dissolved in a solvent for the polymer. Polar solvents, particularly ketonic solvents, such as dioxan, methyl ethyl ketone, and acetone are preferred. The polymer is immediately precipitated from solution by adding a diluent which will dissolve nitric acid and the polymer solvent but in which the polymer will precipitate. Suitable diluents include, chlorinated diluents and hydrocarbon diluents such as, chloroform, methylene chloride, carbon tetrachloride, pentane and hexane. In this manner any nitric acid which remains bound in the polymer is removed. The polymer may then again be washed with a suitable diluent, recovered by any of the common liquid-solid separation means, such as filtration, decantation or centrifugation, and then dried. Procedure B is substantially anhydrous and is preferred when polymers which are sensitive to degradation by hydrolysis are being treated.

The nitration step of either Procedure A or Procedure B may take place in the presence of a water scavenger such as, sulfuric acid, phosphoric acid, boron trifluoride, acetic anhydride or trifluoroacetic anhydride if anhydrous nitric acid is unavailable. Best results are obtained, however, when 100 percent nitric acid is used alone.

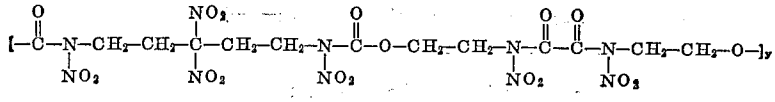
Each step of the above disclosed processes is preferably carried out with agitation. The use of agitation is not critical, but a more even reaction rate is obtained. The pressure under which each step of the above-defined processes may be conducted is preferably atmospheric. Pressure, however, is not critical and increased pressure up to about 500 atmospheres may be employed if desired.

To more clearly illustrate the invention, the following examples are presented. It should be understood that

these examples serve merely as a means of illustrating the invention and should not be construed as limiting the invention to the particular embodiments and conditions set forth therein. Parts and percentages are by weight unless otherwise indicated.

Example I

30 g. of the polyurethane prepared from stoichiometric proportions of 3,3-dinitro-1,5-pentane diisocyanate and N,N'-bis(2-hydroxyethyl)oxamide was added to 600 ml. of 100 percent nitric acid. The solution obtained was maintained at 60°–65° C. for one hour. The solution was cooled to 25° C. and poured into 10 liters of ice-water. The precipitated post-nitrated polyurethane polymer having the formula:



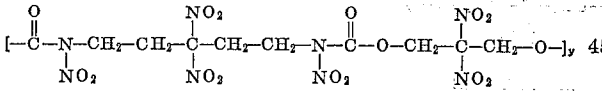
was washed free of acid and dried. The yield was 41.5 g. which was 96.5 percent of theory.

Analysis.—Calculated for $C_{13}H_{16}N_{10}O_{18}$:

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	26.01	2.69	23.33	2,561
Found	26.26	2.78	23.58	2,531

Example II

4.0 g. of the polyurethane prepared from stoichiometric proportions of 3,3-dinitro-1,5-pentane diisocyanate and 2,2-dinitro-1,3-propanediol was added to 40 ml. of 100 percent nitric acid maintained at 0° C. After standing for 30 minutes at 0° C., the nitric acid solution of the polymer was poured into one liter of ice-water. The coagulated product was filtered, washed with a five percent solution of sodium bicarbonate, followed by distilled water and then vacuum dried to a constant weight. The post-nitrated polyurethane polymer having the formula:



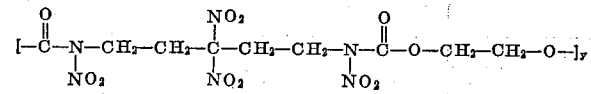
weighed 4.8 g. which was 98 percent of theory.

Analysis.—Calculated for $C_{20}H_{12}N_8O_{16}$:

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	24.01	2.42	22.40	2,320
Found	23.77	2.59	21.63	2,320

Example III

A solution of 5.2 g. of a polyurethane prepared from stoichiometric proportions of 3,3-dinitro-1,5-pentane diisocyanate and ethylene glycol in 55 ml. of 100 percent nitric acid was maintained at 0° C. for thirty minutes. The acid solution was poured into one liter of ice-water and the precipitated post-nitrated polyurethane polymer having the formula:



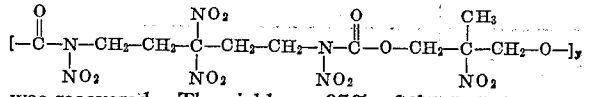
was washed free of acid and dried. Yield, 6.6 g. which was 98 percent of theory.

Analysis.—Calculated for $C_9H_{12}N_6O_{12}$:

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	27.28	3.05	21.21	2,711
Found	27.78	3.05	21.87	2,716

Example IV

The polyurethane prepared from stoichiometric proportions of 3,3-dinitro-1,5-pentane diisocyanate and 2-nitro-2-methyl-1,3-propanediol was dissolved in 100% nitric acid and recovered in accordance with procedure A shown previously. The post-nitrated polyurethane polymer having the formula:

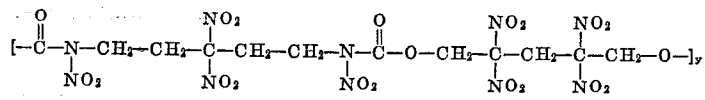


was recovered. The yield was 97% of theory.

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	28.15	3.22	20.90	2,871
Found	28.75	3.27	20.89	2,856

Example V

The polyurethane prepared from stoichiometric proportions of 3,3-dinitro-1,5-pentane diisocyanate and 2,2,4,4-tetranitro-1,5-pentanediol was dissolved in 100% nitric acid and recovered in accordance with procedure A shown previously. The post-nitrated polyurethane polymer having the formula:



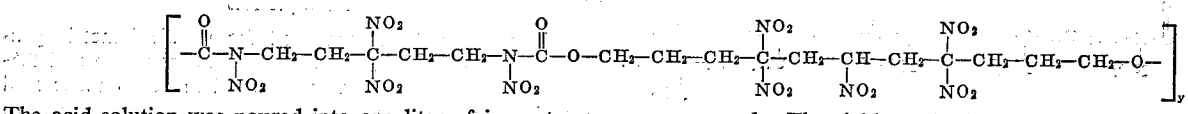
was recovered. The yield was 98% of theory.

Heat of combustion:

	Cal./g.
Calculated	2260
Found	2305

Example VI

The polyurethane prepared from stoichiometric proportions of 3,3-dinitro-1,5-pentane diisocyanate and 4,4,6,8,8-pentanitro-1,11-undecanediol was dissolved in 100% nitric acid and recovered in accordance with procedure A shown previously. The post-nitrated polyurethane polymer having the formula:

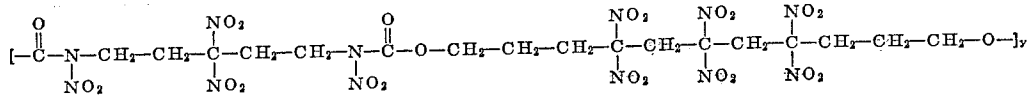


was recovered. The yield was 97% of theory.

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	28.92	3.37	20.62	3,075
Found	29.37	3.41	20.92	3,015

Example VII

The polyurethane prepared from stoichiometric proportions of 3,3-dinitro-1,5-pentane diisocyanate and 4,4,6,6,8,8-hexanitro-1,11-undecanediol was dissolved in 100% nitric acid and recovered in accordance with procedure A shown previously. The post-nitrated polyurethane polymer having the formula;

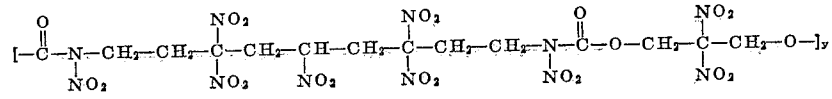


was recovered. The yield was 97% of theory.

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	27.28	3.05	21.21	2,858
Found	27.85	3.12	20.79	2,823

Example VIII

The polyurethane prepared from stoichiometric proportions of 3,3,5,7,7-pentanitro-1,9-nonane diisocyanate and 2,2-dinitro-1,3-propanediol was dissolved in 100% nitric acid and recovered in accordance with procedure A shown previously. The post-nitrated polyurethane polymer having the formula:

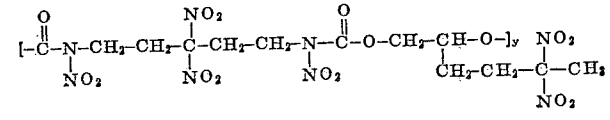


was recovered. The yield was 93% of theory.

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	24.32	2.48	22.29	2,420
Found	24.39	2.39	22.02	2,424

Example IX

The polyurethane prepared from stoichiometric proportions of 3,3-dinitro-1,5-pentane diisocyanate and 5,5-dinitro-1,2-hexanediol was dissolved in 100% nitric acid and recovered in accordance with procedure A shown previously. The post-nitrated polyurethane polymer having the formula:

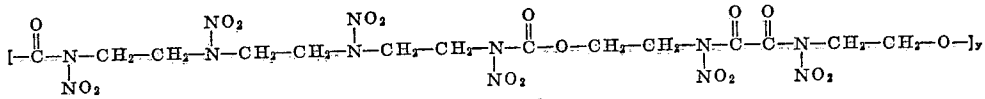


was recovered.

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	28.79	3.35	20.66	3,000
Found	28.83	3.45	21.37	2,996

Example X

The polyurethane prepared from stoichiometric proportions of 3,6-dinitraza-1,8-octane diisocyanate and N,N'-bis(2-hydroxyethyl)oxamide was dissolved in 100% nitric acid and recovered in accordance with procedure A shown previously. The post-nitrated polyurethane polymer having the formula:

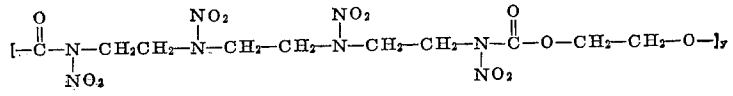


was recovered.

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	26.09	3.13	26.09	2,773
Found	26.41	3.23	25.44	2,799

Example XI

The polyurethane prepared from stoichiometric proportions of 3,6-dinitraza-1,8-octane diisocyanate and ethylene glycol was dissolved in 100% nitric acid and recovered in accordance with procedure A shown previously. The post-nitrated polyurethane polymer having the formula:



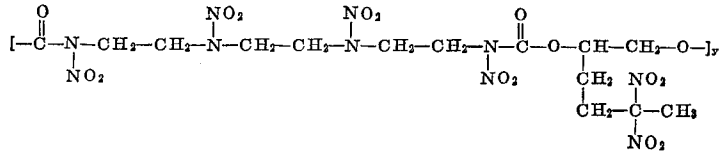
was recovered.

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	27.28	3.66	25.45	3,008
Found	26.63	4.33	25.18	2,979

Example XII

The polyurethane prepared from stoichiometric proportions of 3,6-dinitraza-1,8-octane diisocyanate and 5,5-dinitro-1,2-hexanediol was dissolved in 100% nitric acid and recovered in accordance with procedure A shown

previously. The post-nitrated polyurethane polymer having the formula:

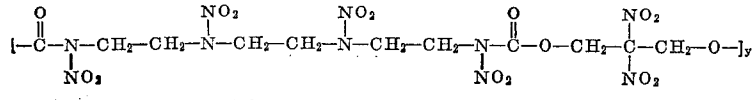


was recovered.

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	28.67	3.78	23.89	3,147
Found	28.88	3.87	24.15	3,148

Example XIII

The polyurethane prepared from stoichiometric proportions of 3,6-dinitraza-1,8-octane diisocyanate and 2,2-dinitro-1,3-propanediol was dissolved in 100% nitric acid and recovered in accordance with procedure B shown previously. The post-nitrated polyurethane polymer having the formula:

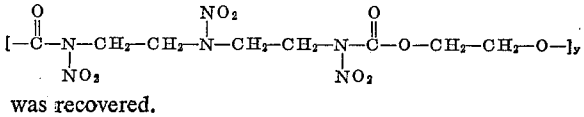


was recovered.

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	23.69	2.65	24.56	2,379
Found	23.10	2.72	23.15	2,377

Example XIV

The polyurethane prepared from stoichiometric proportions of 3-nitraza-1,5-pentane diisocyanate and ethylene glycol was dissolved in 100% nitric acid and recovered in accordance with procedure B shown previously. The post-nitrated polyurethane polymer having the formula:

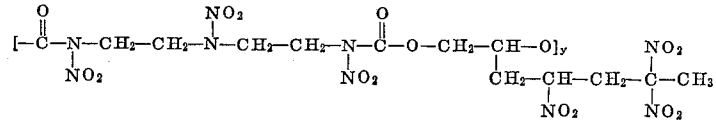


was recovered.

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	27.28	3.43	23.86	2,843
Found	26.41	3.54	23.40	2,832

Example XV

The polyurethane prepared from stoichiometric proportions of 3-nitraza-1,5-pentane diisocyanate and 5,5-dinitro-1,2-hexane-diol was dissolved in 100% nitric acid and recovered in accordance with procedure B shown previously. The post-nitrated polyurethane polymer having the formula:



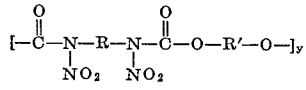
was recovered.

	Carbon, percent	Hydrogen, percent	Nitrogen, percent	Heat of combustion, cal./g.
Calculated	28.92	3.64	22.49	3,054
Found	27.48	3.59	21.16	3,067

Having fully described the compounds, their method of preparation and their utilities, it is desired that the invention be limited only within the lawful scope of the appended claims.

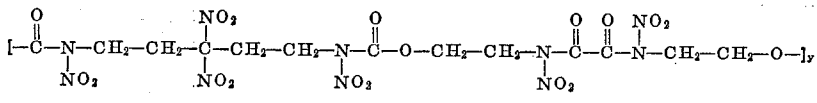
I claim:

1. As compositions of matter, the nitro polyurethanes containing the structural unit:



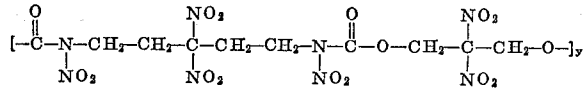
wherein R is a radical selected from the group consisting of lower alkylene, nitroalkylene, nitrazaalkylene, and nitrazanitroalkylene radicals, R′ is a radical selected from the group consisting of lower alkylene, nitroalkylene, nitrazaalkylene, nitrazanitroalkylene ,dialkoxynitroalkylene and dialkyloxamide radicals and y is whole number greater than one.

2. As a composition of matter, the nitro substituted polyurethane containing the structural unit:



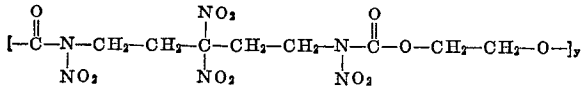
wherein y is a whole number greater than one.

3. As a composition of matter, the nitro substituted polyurethane containing the structural unit:



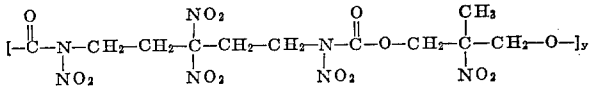
wherein y is a whole number greater than one.

4. As a composition of matter the nitro substituted polyurethane containing the structural unit:



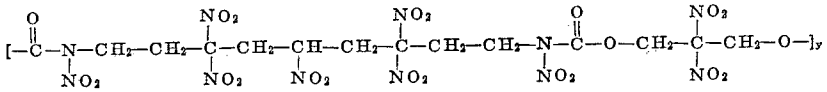
wherein y is a whole number greater than one.

5. As a composition of matter, the nitro substituted polyurethane containing the structural unit:



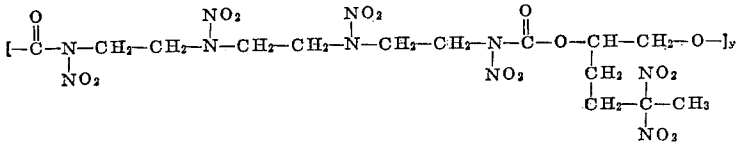
wherein y is a whole number greater than one.

6. As a composition of matter, the nitro substituted polyurethane containing the structural unit:



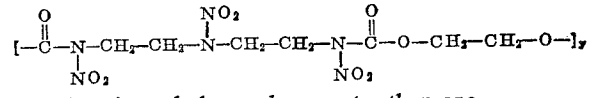
wherein y is a whole number greater than one.

7. As a composition of matter, the nitro substituted polyurethane containing the structural unit:



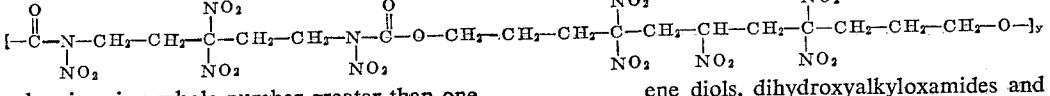
wherein y is a whole number greater than one.

8. As a composition of matter, the nitro substituted polyurethane containing the structural unit:



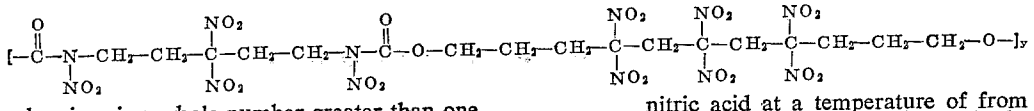
wherein y is a whole number greater than one.

9. As a composition of matter, the nitro substituted polyurethane containing the structural unit:



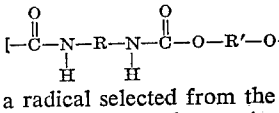
wherein y is a whole number greater than one.

10. As a composition of matter, the nitro substituted polyurethane containing the structural unit:



wherein y is a whole number greater than one.

11. The method of preparing nitro-substituted polyurethane polymers which comprises treating a polyurethane with nitric acid said polyurethane having the formula:



wherein R is a radical selected from the group consisting of lower alkylene, nitroalkylene, nitrazaalkylene, and nitrazanitroalkylene radicals, R′ is a radical selected from the group consisting of lower alkylene, nitroalkylene, nitrazaalkylene, nitrazanitroalkylene, dialkoxynitroalkylene and dialkyloxamide radicals and y is a whole number greater than one.

12. The method of claim 11 which comprises dissolving the polyurethane polymer in an excess of 100 percent nitric acid at a temperature of from about —40° C. to about 65° C., immediately precipitating the polymer by pouring the polymer solution into cold water and recovering the polymer.

13. The process of claim 12 which comprises dissolving the polyurethane polymer in nitric acid at a temperature of 0° C.

14. The process of claim 11 which comprises dissolving the polyurethane polymer in an excess of 100 percent nitric acid at a temperature of about —40° C. to about 65° C., removing the acid by distillation, dissolving the polymer residue in a solvent and immediately precipitating the polymer in a diluent, which will dissolve nitric acid and the polymer solvent but in which the polymer will precipitate, and separating the polymer thus produced.

15. The process of claim 14 which comprises dissolving the polyurethane polymer in nitric acid at a temperature of 0° C.

16. The method of preparing nitro-substituted polyurethane polymers which comprises treating a polyurethane polymer with nitric acid said polymer being prepared by condensing a diisocyanate composition selected from the group consisting of lower alkylene diisocyanates, nitroalkylene diisocyanates, nitrazaalkylene diisocyanates, nitrazonitroalkylene diisocyanates, and mixtures thereof with a diol composition selected from the group consisting of lower alkylene diols, nitroalkylene diols, nitrazaalkylene diols, nitrazanitroalkylene diols, dialkoxynitrazaalkylene diols, dihydroxyalkyloxamides and mixtures thereof.

17. The method of claim 16 which comprises dissolving the polyurethane polymer in an excess of 100 percent nitric acid at a temperature of from about —40° C. to about 65° C., immediately precipitating the polymer by pouring the polymer solution into cold water and recovering the polymer.

18. The process of claim 17 which comprises dissolving the polyurethane polymer in nitric acid at a temperature of 0° C.

19. The process of claim16 which comprises dissolving the polyurethane polymer in an excess of 100 percent nitric acid at a temperature of about —40° C. to about 65° C., removing the acid by distillation, dissolving the polymer residue in a solvent and immediately precipitating the polymer in a diluent, which will dissolve nitric acid and the polymer solvent but in which the polymer will precipitate, and recovering the polymer thus produced.

20. The process of claim 19 which comprises dissolving the polyurethane polymer in nitric acid at a temperature of 0° C.

No references cited.

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