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**HIGH NITROGEN POLYMERS PREPARED BY
REACTING ALDEHYDES WITH AMINOGUA-
NIDINES, TETRAZOLES, OR TRIAZOLES**

Phyllis D. Oja, Walnut Creek, and Earl Thomas Niles,
Danville, Calif., assignors to The Dow Chemical Com-
pany, Midland, Mich., a corporation of Delaware
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This invention is concerned with polymers having a high nitrogen content and more particularly is concerned with organic nitrogen containing polymers having a nitrogen:carbon atomic ratio greater than 1.

It has been demonstrated that high specific impulses, i.e. excellent thrust characteristics, are obtained in rocket propellant systems employing a nitridable fuel and an oxidizing nitrogen source material, i.e. the "B-N" system as disclosed in a copending application Ser. No. 846,509, filed Oct. 14, 1959, since the useful products of the combustion reaction are primarily a solid nitride, hydrogen gas and energy.

However, the overall effectiveness of presently available nitrogen polymeric oxidizing source materials in such systems is reduced by the large amount of carbon present in the molecules. This latter element, as is well understood in the rocket propellant art does not contribute to the desired combustion process and reduces the overall effectiveness of the nitrogen oxidizing source material. Conventional high nitrogen source materials, as presently known to the art, include poly(ethylene hydrazine) and poly(2-methyl-5-vinyltetrazole) both of which have an atomic N:C ratio of 1.

It is recognized in the propellant art that desirably a high nitrogen oxidizing material should have a nitrogen:carbon ratio greater than 2 to insure good performance in a propellant system employing nitrogen as an oxidizer or driving fluid. To illustrate, theoretical calculations indicate that with a boron based fuel, increasing the N:C ratio of a nitrogen oxidizer from 1 to 2 will increase the specific impulse of the system about 10 seconds. Heretofore such high N:C materials have not been available.

It is a principal object of the present invention, therefore, to provide new and novel high nitrogen-containing polymeric materials having nitrogen:carbon ratios of up to about 4.5 or more.

It is a further object of the present invention to provide new and novel high nitrogen containing materials that are relatively stable to atmospheric conditions and which can be handled without rigorous protection from oxygen and moisture.

It is an additional object of the present invention to provide high nitrogen containing materials that are markedly insensitive to impact.

It is another object of the present invention to provide materials having a high nitrogen:carbon ratio that can be easily and safely handled and stored.

It is yet another object of the present invention to provide high nitrogen materials which give physically stable mixtures both with boron based fuels and when used as binders in conventional propellant systems.

It is a further object of the present invention to provide new and novel high nitrogen polymers which can be prepared in relatively simple equipment in easily controlled, safe operations.

The present invention comprises a polymeric composition having repetitive units of a monomeric high nitrogen amine-based material having a minimum N:C ratio of 2 condensed with an aldehyde wherein N:C atom ratio

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of the polymer product ranges from greater than 1 up to about 4.5 or more.

Particularly suitable amine monomers to be employed include for example triaminoguanidine, monoaminoguanidine, diaminotetrazole, diaminoguanidine, 4-amino-3,5-dihydrazino-1,2,4(4H)-triazole, dihydrazinotetrazine, hydrazine, and mixtures of these. These monomers can be employed directly as the free bases or as the azide, hydrochloride, hydrobromide, hydroiodide, nitrate, perchlorate, or acetate salts, for example.

Aldehydes which are employed are formaldehyde, glyoxal, paraformaldehyde, and mixtures of these. Also, reactive derivatives, for example, the acetal, oximes, etc. of these aldehydes can be used.

Generally, commercially available formaldehyde and glyoxal solutions are acidic as obtained. If these are used directly in the polymerization reaction, the resulting polymers are found a N:C ratio reduced from that theoretically calculated. However, unexpectedly it has been found that if the pH of these commercial aldehyde solutions is adjusted, e.g. with ammonia solution, to be from about pH 7 to about pH 9 and preferably from about pH 7 to 7.5 prior to use in the polymerization process the resulting polymer has a N:C ratio substantially the same as calculated.

The mole ratio of reactants, i.e. aldehyde to nitrogen monomer to be used in the repetitive units of the polymer is limited only in the respect that the desired N:C atom ratio is maintained in the polymer product. Ordinarily this ratio will range from about 1 to 4 (amine:aldehyde) and preferably from about 1 to that needed to achieve the predetermined N:C ratio in the polymeric product.

The preparation of the polymer is carried out in a polar or non-polar solvent or solvent mixture. Particularly suitable solvents include, for example, water, methylene chloride, benzene, dimethylformamide, methanol, toluene, mineral spirits, chloroform, ethanol, propanol, ethers, carbon tetrachloride, dioxane or the like and mixtures thereof. Preferably methylene chloride or water will be employed as solvent in the preparation of the instant polymers.

The reaction is carried out over a temperature range wherein the particular solvent employed is in its liquid state. For the illustrated solvent species this range is from about minus 80° to about plus 153° C. At temperatures below the lower value there is substantially no polymer production. At temperatures greater than indicated a very hard, discolored resinous product is produced. Preferably, the reaction will be carried out over a temperature range of from about minus 25 to about plus 100° C.

The reaction can be carried out in low pressure equipment at reduced pressures, i.e. 0.01 millimeter or less mercury absolute or at superatmospheric pressures in appropriate high pressure reactors. However, conveniently the reaction is carried out in ordinary equipment at atmospheric pressures.

The time of reaction is not critical, but ordinarily will be that needed to obtain substantially complete reaction of the reactants into the polymer at the temperature and pressures employed. For most products, a reaction time of from about 1 to about 16 hours is employed.

As indicated hereinbefore the high N:C polymers of the instant invention are used as oxidizing nitrogen source materials in the "B-N" propellant systems employing nitridable fuels.

Also, the instant polymers are very compatible with the ingredients used in the conventional solid propellants, for example, ammonium perchlorate and aluminum. These high nitrogen polymers are extremely useful, therefore, as a binder in present propellant systems. In addition to being compatible with conventional propellant in-

redients, when used as binders with these materials the high nitrogen polymers serve to increase the thrust (specific impulse) of the system and to promote the formation of desirable low molecular weight exhaust gases.

Additionally, these new and novel polymers have general utility as gas generators. Also, they have utility as chemical intermediates.

The following examples will serve to illustrate further the present invention but are not meant to limit it thereto.

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EXAMPLE 1

About 7.3 grams (0.05 mole) of triaminoguanidinium azide and 2 grams (0.05 mole) of formaldehyde were placed in a 50-milliliter three-necked round-bottom flask equipped with a thermometer and connected to a pressure-reducing pump. The formaldehyde was added as an aqueous solution containing about 37.2 percent by weight formaldehyde and had a pH of about 2.

The mixture was heated slowly at atmospheric pressure over a period of one-half hour after which time the mixture temperature had reached about 78° C. and the triaminoguanidinium azide had dissolved. The pressure on the system then was reduced to about 0.1 millimeter mercury absolute and the reaction mix was dried at 78° C. in the presence of anhydrous phosphorus pentoxide for about 16 hours. The resulting polymer was a somewhat brittle, light yellow material which softened over the range of from about 32–70° C. The yield was about 6 grams (71 percent of theoretical). The hygroscopic product analyzed C—17.0 percent, H—6.1 percent and N—77.0 percent. This indicated a N:C atomic ratio of about 3.86 in the molecule.

EXAMPLE 2

A one-liter, round-bottom, three-necked flask fitted with a stirrer, dropping funnel and inlet tube for nitrogen was charged with about 29.4 grams (0.2 mole) of triaminoguanidinium azide and 600 milliliters of methylene chloride. The system was blanketed with nitrogen throughout the operation. The resulting mixture was cooled to about 0° C. and a solution of 13.16 grams (0.16 mole) formaldehyde (37.2 percent by weight in water, pH about 2) and 7.88 grams (0.04 mole) glyoxal (30 percent by weight in water, pH about 2) was added with stirring over one-half hour. The reaction mass was stirred for an additional 1.5 hours at a temperature of about 39° C. After

this time, the solvent was flashed off under reduced pressure at about 50° C. (exterior bath temperature) and the polymer then dried for about 16 hours at about 39° C. substantially in vacuo.

The polymer product was a yellow, somewhat brittle hygroscopic material softening over the range of about 55–80° C. Total recovery was about 32.6 grams, which was essentially quantitative as based on the triaminoguanidinium azide starting material. Elemental analysis indicated C=18.6 percent, H=6.4 percent, N=70.6 percent and N:C atom ratio in the molecule was about 3.26.

EXAMPLE 3

A 500-milliliter, round-bottom, three-necked flask fitted with a stirrer, dropping funnel and inlet tube for nitrogen was charged with about 6.6 grams (0.05 mole) of diaminoguanidinium azide and 200 milliliters of methanol. The system was blanketed with nitrogen throughout the operation. The resulting mixture was cooled to about 4° C. and a solution of 1.5 grams (0.05 mole) of paraformaldehyde in 6 milliliters of methanol was added with stirring over a period of about 15 minutes. The paraformaldehyde solution contained one drop of a 50 percent by weight sodium hydroxide solution to aid dissolution of the aldehyde in the alcohol solvent. The reaction mass was stirred for an additional 165 minutes during which time the reaction temperature was raised to about 53° C. After this time, the solvent was flashed off under reduced pressure at about 50° C. (exterior bath temperature) and the polymer then dried for about 48 hours at room temperature substantially in vacuo.

The polymer product was a yellow somewhat brittle hygroscopic material softening at about 45° C. Elemental analysis indicated C=17.6 percent, H=5.6 percent, N=74.8 percent and the N:C atom ratio in the molecule was about 3.6.

EXAMPLE 4

Following the general procedure as described for the preceding examples, a number of polymers were prepared using a variety of monomeric amines, formaldehyde and/or glyoxal and a solvent.

In these runs a total of one mole of the amine monomers and one mole of aldehyde or aldehyde mixture were reacted. The amine and aldehyde components were selected to give a number of polymers having different, predetermined N:C ratios.

The results of these runs are presented in Table 1 which follows:

TABLE 1

Run No.	Amine ¹ Composition	Parts by weight	Aldehyde ² Aqueous (Parts by weight)		Solvent	Polymer Product (N/C Ratio)
			Formaldehyde ³	Glyoxal ³		
1.....	Triaminoguanidinium-Azide.....	1	4	1	CH ₂ Cl ₂	3.3
2.....	do.....	1	4	1	H ₂ O.....	2.7
3.....	do.....	1	1	1	CH ₂ Cl ₂	1.6
4.....	do.....	1	1	1	CH ₂ Cl ₂	2.4
5.....	do.....	1	4	1	Dimethylformamide.....	3.0
6.....	do.....	1	4	1	H ₂ O.....	3.8
7.....	Triaminoguanidine.....	1	4	1	CH ₂ Cl ₂	2.2
8.....	Triaminoguanidinium-HCl.....	1	1	1	CH ₂ Cl ₂	2.1
9.....	Diaminoguanidinium-HCl.....	1	1.43	1	CH ₂ Cl ₂	1.9
10.....	Amino-dihydrazino-Triazole-HCl ⁴	1	1	1	CH ₂ Cl ₂	2.3
11.....	Amino-dihydrazino-Triazole.....	1	4	1	CH ₂ Cl ₂	3.2
12.....	Triaminoguanidinium-Azide.....	4	4	1	CH ₂ Cl ₂	2.4
13.....	Hydrazine Azide.....	1	4	1	CH ₂ Cl ₂	2.5
14.....	Triaminoguanidinium-Azide.....	4	4	1	CH ₂ Cl ₂	2.3
15.....	Urea.....	1	4	1	CH ₂ Cl ₂	2.3-2.5
16.....	Triaminoguanidinium-Azide.....	1	4	1	CH ₂ Cl ₂	2.0-2.1
17.....	Amino-dihydrazino-Triazole.....	1	4	1	CH ₂ Cl ₂	4.4
18.....	Triaminoguanidine.....	1	4	1	CH ₂ Cl ₂	3.6
19.....	Amino-dihydrazino-Triazole.....	1	4	1	CH ₂ Cl ₂	3.9
20.....	Triaminoguanidine.....	1	4	1	CH ₂ OH.....	4.3

¹ Total one mole.

² 37.2 percent by weight in water. Solution as used about pH 2.

³ 30 percent by weight in water. Solution as used about pH 2.

⁴ 4-amino-3,5-dihydrazino-1,2,4(4H)-Triazole-Hydrochloride.

⁵ Adjusted to pH 7 prior to use.

⁶ Adjusted to pH 9 prior to use.

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In a manner similar to that described for the foregoing examples monoaminoguanidinium hydrobromide and the oxime of glyoxal can be reacted in the presence of benzene solvent to prepare the corresponding high nitrogen polymer. Diaminotetrazole·HNO₃ can be polymerized with methylal in toluene to give a high nitrogen polymer having a predetermined N:C ratio. Dihydrazinotetrazine can be condensed with formoxime in diethyl ether to give the corresponding high nitrogen polymer.

Various modifications can be made in the present invention without departing from the spirit or scope thereof for it is understood that we limit ourselves only as defined in the appended claims.

We claim:

1. A nitrogen containing organic polymer having a nitrogen:carbon atom ratio of from greater than 1 to about 4.5 which comprises repetitive units of from about 1 to 4 molar equivalents of

(a) a member selected from the group consisting of monoaminoguanidine, diaminoguanidine, triaminoguanidine, diaminotetrazole, 4-amino-3,5-dihydrazino-1,2,4(4H)-triazole, dihydrazinotetrazine, mixtures thereof and the acid addition salts thereof condensed with about 1 molar equivalent of

(b) an aldehyde based compound selected from the group consisting of formaldehyde, glyoxal, paraformaldehyde, formaldehyde-glyoxal mixtures, acetals of formaldehyde, glyoxal, paraformaldehyde and formaldehyde-glyoxal mixtures and oximes of formaldehyde, glyoxal, paraformaldehyde and formaldehyde-glyoxal mixtures.

2. A brittle, thermoplastic nitrogen-containing organic polymer having a nitrogen:carbon atom ratio of from about 2.5 to about 4.5 which comprises the condensation product of a mole equivalent of triaminoguanidinium azide with a mole equivalent of formaldehyde.

3. A brittle, thermoplastic nitrogen-containing organic polymer having a nitrogen:carbon ratio of about 3 which comprises the condensation product of a mole equivalent of triaminoguanidinium azide with a mole equivalent mixture of formaldehyde and glyoxal.

4. A brittle, thermoplastic nitrogen-containing organic polymer having a nitrogen:carbon atom ratio of about 4 which comprises the condensation product of a mole equivalent of diaminoguanidine azide with a mole equivalent of formaldehyde.

5. A brittle, thermoplastic nitrogen containing organic polymer having a nitrogen:carbon ratio of about 3.6 which comprises the condensation product of a mole equivalent of diaminoguanidinium azide with a mole equivalent of paraformaldehyde.

6. A process for preparing nitrogen containing organic polymers having a predetermined nitrogen:carbon atom ratio of from greater than 1 up to about 4.5 which comprises

(a) contacting from about 1 to about 4 molar equivalents of a member selected from the group consisting of

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- (1) monoaminoguanidine
- (2) diaminoguanidine
- (3) triaminoguanidine
- (4) diaminotetrazole
- (5) 4-amino-3,5-dihydrazino-1,2,4(4H)-triazole
- (6) dihydrazinotetrazine
- (7) mixtures of hereinbefore listed amines
- (8) acid addition salts of the hereinbefore listed amines

with from about 1 molar equivalent of a member selected from the group consisting of

- (1) formaldehyde
- (2) glyoxal
- (3) formaldehyde-glyoxal mixtures
- (4) acetals of formaldehyde
- (5) acetals of glyoxal
- (6) oximes of formaldehyde
- (7) oximes of glycol
- (8) paraformaldehyde
- (9) acetals of paraformaldehyde
- (10) oximes of paraformaldehyde
- (11) acetals of formaldehyde-glyoxal mixtures
- (12) oximes of formaldehyde-glyoxal mixtures.

in the presence of a solvent selected from the group consisting of

- (1) water
- (2) methylene chloride
- (3) benzene
- (4) dimethyl formamide
- (5) methanol
- (6) ethanol
- (7) toluene
- (8) diethyl ether

(b) reacting the mixture from about 1 to about 16 hours at a temperature where the solvent member is in its liquid form

thereby to condense the amine and the aldehyde into the corresponding polymer having a preselected nitrogen:carbon ratio.

7. The process as defined in claim 6 wherein the aldehyde as employed is at a pH of from about 7 to about 7.5.

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