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[54] **PROPELLANT BINDER**  
**12 Claims, No Drawings**  
 [52] **U.S. Cl.**..... **260/32.4,**  
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 149/102, 260/2, 260/29.1, 260/30.6, 260/31.4,  
 260/31.6, 260/31.8, 260/33.2, 260/78, 260/78.4,  
 260/80, 260/583, 260/584, 260/836  
 [51] **Int. Cl.**..... **C08f 45/44,**  
 C08g 51/44

**ABSTRACT:** This invention relates to solid propellant formulations. More particularly, it relates to a novel binder for utilization in such solid propellants.

## PROPELLANT BINDER

Solid propellants found in application today are divided into two distinct categories; double-base propellants and composite propellants. The distinction is based on the physical characteristics of the propellants and their composition. Most propellants contain a sufficient amount of oxygen such that upon ignition they can be readily burned and converted to gaseous product. Thus, without any additional source of oxygen a solid propellant can sustain continuous burning producing a great amount of pressure to be utilized in producing thrust.

In general, a double-base propellant contains as its principle ingredient, nitrocellulose, and an explosive plasticizer normally nitroglycerin. Double-base propellants can contain inert plasticizers, stabilizers, ballistic modifiers and other high energy materials which may, in fact, be highly explosive themselves. The composite propellants embrace a solid particulate oxidizer material dispersed throughout a matrix of plastic or resinous-type material. The matrix may provide the fuel for the combustion, however, normally today a solid particulate fuel is dispersed within the matrix. This fuel is normally a finely ground metal or metal wire. The composite propellants are also known as hydrocarbon systems because of the normally hydrocarbon binder material used. The three types of binders previously used in these hydrocarbon systems include polyurethane, polybutadiene-acrylic acid or PBAA and more recent, carboxy-terminated linear polybutadiene. Use of these binders, as well as the double-base system binders, often introduces several problems.

Particularly concerned with the processing of the propellant, data has indicated that double-base systems based on nitrocellulose and high energy plasticizers such as trimethylolethanetrinitrate or triethyleneglycoldinitrate with oxidizers such as ammonium perchlorate, hydrazine nitroform or nitronium perchlorate and fuels such as aluminum hydride can produce very high specific impulses. However, in processing it is difficult to obtain the necessary level of solids loading in the double-base system. That is, it is often impossible to incorporate successfully the high percentages of the solid particulate oxidizer and fuel necessary to produce the theoretical impulse that could be derived from such a system. Additionally, double-base systems are characterized by the extreme sensitivity to impact. This results in a serious drawback in the processing of such propellants due to the extreme danger in handling.

With regard to the composite propellants, the presence of polyurethane, polybutadiene acrylic acid or carboxy-terminated linear polybutadiene binders require very high total solids loading to achieve desired high impulse goals. However, the impact sensitivity of the final propellant is much lower than that of the double-base systems and thus processing from the sensitivity standpoint is improved. Generally, though, the impulse to be derived from the composite systems is lower than that obtained from the double-base ones.

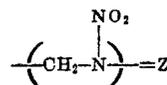
On the basis of performance, it is apparent that the highest impulse is obtainable only with a double-base binder. There is generally little difference among the hydrocarbon systems except that higher solids loading is possible with the carboxy-terminated linear polybutadiene binder. However, it is much more difficult to achieve desired high impulse with the hydrocarbon binders. From a safety point, the hydrocarbon binders appear to be considerably superior to the double-base ones. Processing problems are normal with the double-base binder but are more difficult with the hydrocarbon ones due to the fact that the high total solids loading is required to obtain high impulse.

Thus, it is an object of this invention to provide a novel propellant binder system having high performance with regard to specific impulse.

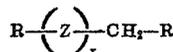
Another object of this invention is to provide a solid propellant binder that has good safety for handling and processing.

A further object of the invention is to provide a new solid propellant binder having ease of processing.

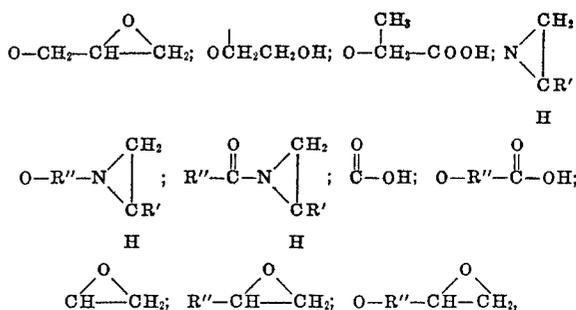
The above and other objects are accomplished by a binder system based upon a linear polymethylenenitramine. The nitramine backbone has the following formula which will be represented as Z:



It may appear from two to six times in the monomers utilized to prepare the final polymeric product. It is preferred that it appear three times in the monomer. The monomers that will form the polymeric binder of this invention have the following general formula:



Wherein  $x$  may vary from two to six and  $R$  is a functional group capable of entering into cross-linking or polymerization. Thus,  $R$  can be selected from the class consisting of:

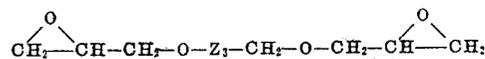


wherein  $R$  is selected from the class consisting of H and  $\text{CH}_3$ , and  $R''$  is an alkylene radical of from one to five carbon atoms.

Because of the preferred method of synthesis of the monomers,  $R$  is normally a substituted alkoxy group. Thus, an ether linkage is normally present connecting the terminal group to the backbone. Additionally, an ester linkage can be formed instead of the ether using a carboxy acid instead of an alcohol in the synthesis of the monomers, however, this type of ester linkage is less desirable than the ether one from the standpoint of hydrolytic stability. The preferred terminal functional groups capable of chain extension and polymerization which are present on the  $R$ 's are the epoxy, carboxy and hydroxy groups because of their ease of cross-linking to form good propellant binders. The number of carbon atoms in the  $R$  chain should be kept generally to a minimum, preferably not more than four though up to six may be usable. A resin having the minimum number of carbon atoms is desired to produce a polymer having the highest percentage of the nitramine backbone to give high energy. The presence of the carbon atoms will tend to detract from this desired property.

It is important in the formation of solid propellant binders that in the polymerization reaction there be no condensation material which must be removed from the propellant. As a result, the particular terminal functional groups present must be ones which are capable of entering into an addition-type polymerization so that no byproducts such as water or the like are formed which would deleteriously effect the propellant.

It is found that particularly good results are obtained when one of the monomers that is reacted to form the polymeric binder of the invention is a compound having epoxy terminal groups. The most preferred monomer having the epoxide end groupings is 1,2,14,15-diepoxy-4,12-dioxo-6,8,10-trinitrazapentadecane having the following formula:



This monomer may in turn be reacted with another monomer having the nitramine backbone and having one of the func-



acid can be from 0 to 100 percent. Any of the monomers of the invention can be extended and cross-linked by the addition of various known cross-linking additives which are capable of reacting with the terminal groups present on the nitramine monomers. Additionally, linear polymers can be formed by the reaction of two of the nitramine monomers having terminal groups capable of polymerization with each other. The resultant linear polymers will generally only have one reactive site on each end and cannot cross-link. As a result, to accomplish such cross-linking, it is generally necessary to add an agent capable of causing such a transpire.

When the preferred diepoxide monomer is reacted with a dicarboxy-terminated monomer, citric acid may be used as a cross-linking agent. Other cross-linking agents include: 1,2,3,4-butane tetracarboxylic acid, trimesic acid, trimellitic acid and 1,2,3-propane tricarboxylic acid. It should be apparent that not all of the above cross-linking agents are compatible with all the nitramine monomers of the invention. The method of selecting the proper cross-linker is well within the skill of the art. As the selection of appropriate nitramine monomers, the choice of a cross-linking agent is based on ones that can react with the terminal functional group of the nitramine monomers forming an addition-type polymer.

The proportion of the three ingredients is dependent on the end functional groups of each. It is desirable that substantially all of the end functional groups are reacted. For example, the ratio of epoxy to carboxy equivalents would for most practical formulations be from 1:1 to 4:1. The amount of cross-linker present can be from 0 to 100 percent of total carboxy equivalents present depending on properties desired.

When the preferred diepoxide is used with a nitramine diol and an anhydride, maleic anhydride being preferred, a cross-linked polymer is formed. The anhydride reacts with the diol to form a dicarboxy acid which then reacts with the diepoxide. This polymerization would give only a linear polymer except that when the ester linkage is made, a hydroxy group is produced which can react with excess anhydride to form a carboxy group along the chain for a cross-linking site. Other usable anhydrides include: phthalic anhydride, hexahydrophthalic anhydride, succinic anhydride and glutaric anhydride.

It should be apparent that not all of the above anhydrides are compatible with all the nitramine monomers of the invention. The method of selecting the proper anhydride is well within the skill of the art. This anhydride must primarily be an anhydride of a dicarboxy acid. The proportion of the three ingredients is dependent on the end functional groups of each. It is desirable that substantially all of the end functional groups are reacted. For example, the ratio of equivalents of diol: maleic anhydride: diepoxide are 1:0.75-2:1-3 for the most practical formulations.

The metal fuel may constitute 0.2 to 32 weight percent propellant grain of this invention, preferably is one or more of the metals of Groups I-A, II-A, III-A and Groups I-B through VII-B, and Group VIII of the Periodic Table. Thus, the metal may be Group I-A elements such as lithium, and Group II-A metals such as beryllium or magnesium. Illustrative of the Group III-A metals is aluminum. The metals of Group I-B through VII-B include copper, silver, zinc, cadmium, titanium, zirconium, vanadium, niobium, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, ruthenium, rhodium, osmium, palladium, and platinum. Additionally, hydrides of the metals such as beryllium hydride and aluminum hydride are contemplated.

To aid in the processing of the propellant, it is often advisable to employ plasticizers in the preparation and utilization of the polymeric and plastimeric materials employed in the invention. The plasticizers can be up to 75 percent by weight of the binder composition. It is preferred that energetic plasticizers be used with the polymers of this invention to give higher impulse. Such preferred ones include the nitroplasticizers such as bis-dinitropropylformal, bis-dinitropropylacetal, and 2,2-nitro propane. Other plasticizers

may be of the general type of inert and explosive plasticizers. Examples of inert plasticizers include triacetin, the various phthalates such as diethyl phthalate, dibutyl phthalate, dioctyl phthalate, di-(methoxyethyl) phthalate, methyl phthalyl ethyl glycolate, ethyl phthalyl ethyl glycolate and butyl phthalyl butyl glycolate, sebacates such as dibutyl and dioctyl sebacates, adipates such as dioctyl adipate and di(3,5,5-trimethylhexyl)adipate, glycol esters of higher fatty acids, organic phosphate esters such as tributoxylethyl phosphate, and the like. The explosive plasticizers include nitroglycerin, butane triol trinitrate, diglycol dinitrate, ethylene glycol dinitrate, and the like.

The solids oxidizing agents utilized can be compounds such as metal perchlorates and metal nitrates. The metal perchlorates employed as oxidizing agents or oxygen carriers in the compositions are anhydrous and have the general formula  $M(ClO_4)_x$  wherein M is  $NH_4$  or a metal and x is the valence of M. Since the propellant composition is required to withstand high-temperature storage, it is preferable that the melting point and the decomposition temperatures of the oxidizer be as high as possible. The perchlorates of the Group I-A, Group I-B, and Group II-A metals are found to have the required high-temperature stability and are employed in the preparation of propellant compositions by the process of this invention. Hence, the metal perchlorates used in the preparation of the propellant compositions include lithium perchlorate, sodium perchlorate, potassium perchlorate, rubidium perchlorate, and cesium perchlorate which are the perchlorates of the metals of Group I-A of the Periodic Table of Elements; silver perchlorate which is a perchlorate of the Group I-B metal; and magnesium perchlorate, calcium perchlorate, strontium perchlorate, and barium perchlorate which are the perchlorates of the Group II-A metals. In addition to the metal perchlorates, the compounds ammonium perchlorate and nitronium perchlorate find extensive use in propellant compositions. Examples of the nitrates of the Group I-A, and I-B and II-B which are employed in preparing propellant compositions by the process of this invention are compounds such as lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, calcium nitrate, barium nitrate, strontium nitrate, etc. Ammonium nitrate is also used. The amount of oxidizer present falls within the range of 25 to 80 weight percent of the propellant composition.

The ratio of total solids-to-polymeric binder material in a propellant falls in the range of from about 1:1 to about 9:1 with an optimum ratio of about 7:3.

Other substances which are employed in the preparation of propellants by the process of this invention include minor amounts of burning catalysts, well known in propellant compositions. These are composed of one or a mixture of two or more metal oxide powders in amounts sufficient to improve the burning rate of the composition. The amounts usually range from about 0.01 to about 3 weight percent, based on the weight of the oxidizer employed. The particle size of the powders can range from about 10 to about 250 microns in diameter. Nonlimiting examples of metals that serve as burning catalysts are copper, vanadium, chromium, silver, molybdenum, zirconium, antimony, manganese, iron, cobalt, and nickel. Examples of metal oxide burning catalysts are ferric oxide, aluminum, copper oxide, chromic oxide, as well as the oxides of other metals mentioned above.

Burning rate depressants and modifiers are also sometimes advantageously added to the solid propellant grain of this invention. These are generally compounds added in the amounts of 0.05 to 5 weight percent of the propellant composition. These compounds tend to inhibit burning reaction rates or absorb heat and include specifically carbonyl chloride, oximide, nitroguanidine, guanidine nitrate, and oxalic acid.

Curing catalysts are often added in minor amounts to cure the polymer in the performance of the process of this invention. Nonlimiting examples of catalysts used for this purpose are aluminum chloride, tris(trimethylsilyl) borate, benzoyl peroxide, and other catalysts well known in the curing of

plastics, resin, polymers, and rubbers. Examples of various catalysts may be found in text books such as "Synthetic Rubber," by G. S. Whitley, pp. 892-933, 1954 Ed., published by John Wiley and Sons, Inc., New York. The curing catalysts are added in amounts of from 0.1 to about 10 weight percent based on the weight of the polymer, resin or elastomer. The particular catalyst and amount employed depend on the state of cure desired and the nature of the polymeric material employed in the composition.

The following example indicates the preparation of a propellant formulation utilizing the polymeric binder of this invention.

### EXAMPLE II

The following constituents were utilized to form the propellant grain.

| Binder           | Grams |
|------------------|-------|
| TNDE             | 38.90 |
| Maleic anhydride | 4.78  |
| TNDO             | 13.48 |
| BDNPF-BDNPA      | 40.30 |

(Mixture 50 percent: 50 percent of bis-dinitropropylformal: bis-dinitropropyl acetal)

| Oxidizer             | Grams |
|----------------------|-------|
| Ammonium perchlorate | 149.3 |
| Aluminum             | 78.0  |

All of the binder ingredients are placed in a vertical or horizontal mixer such as the Baker-Perkins mixer which has been previously heated to 150°-175° F. The binder ingredients were then mixed for a period of time sufficient to wet all the ingredients. Vacuum is then placed on the mixer and mixing is continued for 20 minutes. At this point, the mix was very fluid and transparent. The aluminum powder is then added and mixed until wet. Vacuum was then placed on the mixer and mixing was continued for about 2 minutes until the aluminum was thoroughly dispersed. The mixer was then stopped and the oxidizer was added in three equal increments. After each of the first two increments, the ingredients were mixed for 10 minutes under vacuum. After the last increment of oxidizer was added, the final ingredients were mixed for 30 minutes under vacuum. The mixer is then finally stopped and the ingredients are ready for pouring into a mold to be cast. The propellant mixed is poured into a mold and cured at atmospheric pressure at 24 to 120 hours at 120° F.

### EXAMPLE III

The process of manufacturing propellant as set forth in above example II was repeated, utilizing the following formulation. The only difference from the process of example II was between 20 and 50 p.s.i.g. pressure was used when curing the material.

| Propellant LCH-35           | Percent | Grams   |
|-----------------------------|---------|---------|
| TNDE                        | 11.27   | 225.6   |
| TNDA                        | 4.10    | 82.0    |
| Citric acid                 | 0.33    | 6.4     |
| Diethylene glycol dinitrate | 14.17   | 283.4   |
| Resorcinol                  | 0.13    | 2.6     |
| Ammonium perchlorate        | 68.00   | 1359.00 |
| Aluminum                    | 2.00    | 40.00   |

In this example it is noted that nitrate ester plasticizer was used. The plasticizer was stabilized with the presence of a small amount of resorcinol.

### EXAMPLE IV

A more preferred propellant formulation due to physical properties of cured propellant is shown below. It was prepared in accord with the procedure of example II.

| Propellant CLH-43-1                           | Percent | Grams  |
|---|---------|--------|
| TNDE  | 13.42   | 402.6  |
| Citric acid                                   | 2.28    | 68.4   |
| Petrin (plasticizer pentaerythritol)          | 14.00   | 420.0  |
| Ethyl centralite (stabilizer for plasticizer) | 0.30    | 9.0    |
| Ammonium perchlorate                          | 46.0    | 1380.0 |
| Aluminum                                      | 24.0    | 720.0  |

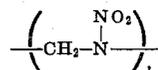
Several 2-inch and 6-inch rocket motors were made utilizing the formulations set forth in the previous examples as well as varying the relative proportion of the constituents so as to obtain range of properties for the grains. Typical properties obtained from the formulation tested follow:

| Mechanical Properties            |             |
|----------------------------------|-------------|
| Elongation, $e_m$ , percent      | 11-37       |
| Tensile Strength, $S_m$ , p.s.i. | 95-260      |
| Modulus E, p.s.i.                | 520-3400    |
| Density, lb.-cu.-in.             | 0.063-0.068 |
| Impact Sensitivity, in.-lb.      | 13-32       |
| Burning Rate, in.-sec.           |             |
| 500 p.s.i.a.                     | 0.178-0.266 |
| 1000 p.s.i.a.                    | 0.229-0.351 |
| Pressure Exponent, $n$           | 0.34-0.40   |

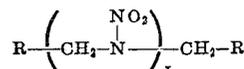
Although the invention has been described and illustrated in detail, it is to be clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of this invention being limited only by the terms of the appended claims.

We claim:

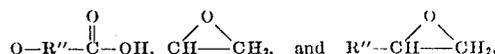
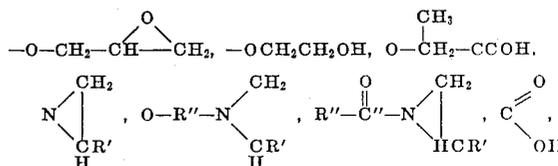
I. Polymers having the backbone



, said polymer formed from the addition polymerization of monomers having the formula:



wherein  $x$  is a whole integer from two to six and  $R$  is selected from the class consisting of:



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wherein  $R'$  is selected from the class consisting of H and  $\text{CH}_3$  and  $R''$  is an alkylene radical of from one to five carbon atoms.

2. The polymer of claim 1 further polymerized with a compound capable of entering into addition polymerization to cross-link said polymers.

3. The polymer formed from the reaction of 1,2,14,15-diepoxy-4,12-dioxa-6,8,10-trinitrazapentadecane with 3,11-dioxa-5,7,9-trinitrazatridecane-1,13-diol.

4. The polymer formed from the reaction of 1,2,14,15-diepoxy-4,12-dioxa-6,8,10-trinitrazapentadecane with 3,11-dioxa-5,7,9-trinitrazatridecane-1,13-dicarboxyl.

5. The polymer formed from the reaction of 1,2,14,15-diepoxy-4,12-dioxa-6,8,10-trinitrazapentadecane with 3,11-dioxa-5,7,9-trinitrazatridecane-1,13-diol and maleic anhydride.

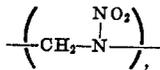
6. The polymer formed from the reaction of 1,2,14,15-diepoxy-4,12-dioxa-6,8,10-trinitrazapentadecane with 3,11-dioxa-5,7,9-trinitrazatridecane-1,13-dioic acid and citric acid.

7. The polymer of claim 5 wherein the ratio of diol:anhydride:diepoxide is within the range 1:0.75-2:1-3.

8. The polymer of claim 6 wherein the ratio of dioic acid: citric acid: diepoxide is 1:0.25-2:1-3.

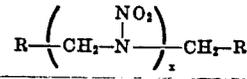
9. The polymer formed from the reaction of 1,2,14,15-diepoxy-4,12-dioxa-6,8,10-trinitrazapentadecane with citric acid.

10. A solid propellant binder composition comprising:  
a polymer having the backbone

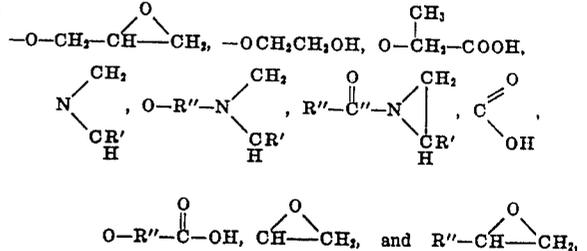


, said polymer formed from the addition polymerization of monomers having the formula:

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wherein  $x$  is a whole integer from two to six and  $R$  is selected from the class consisting of:



wherein  $R'$  is selected from the class consisting of H and  $\text{CH}_3$  and  $R''$  is an alkylene radical of from one to five carbon atoms,

a cross-linking agent for said polymer.

11. The binder of claim 10 additionally comprising:

a plasticizer is an amount up to 75 weight percent of the binder composition.

12. The binder of claim 11 wherein said plasticizer is a nitroplasticizer selected from the class consisting of: bis-dinitropropylformal, bis-dinitropropylacetal, and 2,2-nitropropane.

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