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3,418,183

PROPELLANT COMPRISING HYDRAZINE NITROFORM STABILIZED WITH DICARBOXYLIC ACID ANHYDRIDE

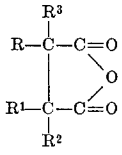
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20 Claims. (Cl. 149—6)

This invention concerns the stabilization of propellant oxidizers and the propellant compositions derived therein.

More particularly, this invention relates to a method of stabilizing hydrazine nitroform and to various high energy formulations containing this oxidizer.

The novel stabilizing agents of this invention are the anhydrides of dicarboxylic acids of the formula:



wherein R, R^1, R^2 and R^3 which can be the same or different are selected from the group consisting of hydrogen, alkyl, alkenyl, arylalkyl and arylalkenyl radicals, straight chain or branched chain, joined or conjoined.

Illustrative stabilizing agents or as they are alternatively referred to anti-gassing agents include among many others, alkyl and alkenyl compounds such as methyl succinic anhydride, ethyl and ethenyl succinic anhydrides, the propyl and propenyl succinic anhydrides, the butyl and butenyl succinic anhydrides, the pentyl and pentenyl succinic anhydrides, the hexyl and hexenyl succinic anhydrides, the heptyl and heptenyl succinic anhydrides, the octyl and octenyl succinic anhydrides, as well as the higher homologues such as dodecyl and dodecenyl succinic anhydrides, the heptadecyl and heptadecenyl succinic anhydrides and the like. Also contemplated as being within the scope of this invention are the corresponding alkyl- and alkenyl-aryl succinic anhydrides such as the hexyl and hexenyl phenyl succinic anhydrides, the octyl and octenyl phenyl succinic anhydrides and the like.

Hydrazine nitroform is known throughout the propellant art as an exceedingly potent oxidizer. Unfortunately in typical propellant formulations it shows a strong tendency to bubble, or as it is called in the art, to "gas." When gassing occurs the resultant solid propellant composition contains cracks and voids and frequently overflows the motor casing. These flaws adversely affect the propellant's properties and prevent its being used. For example, physical properties are generally poor, burning rates are erratic and consequently specific impulses are not reproducible. As a result of this erratic performance, commercially available hydrazine nitroform has had only limited use in propellant formulations.

The gassing tendency of hydrazine nitroform (HNF) has been attributed to impurities. Unfortunately there is little agreement as to which impurities are the prime cause of HNF's gassing. In addition any extensive purification of commercial HNF product would certainly raise its cost substantially and make its use as an oxidizer less attractive. This would especially be true where its use in commercial applications such as gas generating devices are contemplated.

Stabilizing agents such as mercurous oxalate have been suggested but these agents are largely directed to control the relatively high impact sensitivity of the oxidizer rather than its gassing tendencies. Because of the failings of commercial grade HNF as a propellant oxidizer and

the difficulty and expense in ascertaining what impurities, if any, are the causitive factor in its gassing, there is a real need for the development of anti-gassing additives for use in commercial grade HNF oxidizer. These anti-gassing additives ideally would be inexpensive, would minimize HNF gassing, assure reproducible burning and propulsion and could be used in commercially available HNF without additional modifications.

Thus, it is a salient object of this invention among others to disclose novel anti-gassing additives for hydrazine nitroform and methods for their use.

A more general object of this invention is to develop a novel class of anti-gassing additives useful in the prevention of gassing in solid propellants generally.

A further object and a related aspect of this invention is the development of novel hydrazine nitroform-carborane solid propellant formulations.

These objects among others are accomplished by the inventive process and compositions described more fully below.

In practice a novel and superior gas-generating composition is prepared by mixing, casting, and curing a curable homogenous composition composed of (1) an oxidizer (2) a combustible fuel binder (3) the novel stabilizing or anti-gassing agents of this invention with or without (4) diverse propellant adjuvants.

The formulated propellant composition of this invention is composed essentially of:

(1) From about 20–85% by weight of an hydrazine nitroform oxidizer preferably 50–85% by weight of this oxidizer, optionally supplemented by other oxidizers such as the perchlorates.

(2) From about 10–50% by weight of a combustible fuel binder. The combustible fuel binder always includes a major amount of a polymeric composition and a minor amount of one or more curing agents. The preferred binders are the carboxyl-terminated carborane polyesters and the carboxyl-terminated polyalkadienes such as the carboxyl terminated polybutadienes. Less preferred but superior binders are the carboxyl-terminated linear polyesters, the polyester-polyurethane copolymers and the polyester-polyurethane polymers terminated with thiol groups. Other polymers which can be used are the polycarbonates, polyurethanes, the polyacrylates, the polyepoxides as well as the copolymers of one or more of these.

(3) From about 1–10% by weight of one or more of the novel stabilizers (anti-gassing additives) of this invention. Substantial reduction in gassing is observed when this stabilizing amount of one or more or the stabilizing dicarboxylic anhydrides are incorporated into the propellant composition. The preferred stabilizers are the alkenyl succinic anhydrides particularly those in the liquid state such as dodecenyl succinic anhydride and its homologues.

(4) Up to 30% by weight of a propellant adjuvant. As indicated earlier, the presence of propellant adjuvants while not essential to the operability of the inventive propellant compositions, are preferable to achieve optimum performance. Where such an adjuvant is used, it will ordinarily comprise between about 0.25–25% by weight of the propellant composition. These include the alkaline earth among other oxides, ignition catalysts such as aluminum, lithium, boron and the like among others.

The above components of the propellant mixture are blended to form a homogeneous composition, then cast or extruded, and cured using the procedures well known in the propellant art so that they will burn evenly and continuously. Ordinarily the curing is conducted between 60 to 150° F. for periods ranging up to 96 hours or more. Since the final propellant composition contains at least several ingredients, it is essential for satisfactory perfor-

mance that the composition be homogeneous in content. Thus throughout this disclosure and claims, the propellant composition referred to is understood to be one that has been formulated to be homogeneous.

(1) OXIDIZER

As indicated earlier the hydrazine nitroform oxidizer, combustible fuel binder and propellant adjuvants can be varied both as to content and choice. For example, numerous perchlorates including ammonium perchlorate, nitronium perchlorate, the alkaline earth metal perchlorates and the alkali metal perchlorates among other metallic perchlorates can be used as oxidizers to supplement the hydrazine nitroform oxidizer. However, unmodified hydrazine nitroform is the favored perchlorate oxidizer primarily because it produces more energetic formulations and when stabilized burns evenly. In addition, it is available in large quantities in a high state of purity at relatively low cost.

In general, varying proportions of the oxidizer can be employed in the propellant compositions of this invention. For example, depending upon the use intended, the oxidizer can be present in the cured propellant composition in sufficient quantity so that it makes up about 20–80% by weight of the finished compositions.

Compositions containing the lower percentage of oxidizer, in the range of 20–50%, have a lower burning rate and thus would be useful for gas turbine and jet aircraft starters; whereas the compositions containing the higher percentage (about 50–80% by weight) of oxidizer would be useful in preparing gas generating or propellant compositions where a higher burning rate is desirable.

(2) FUEL BINDER

The fuel referred to throughout this application refers to combustible polymeric resins or their precursors which can be cured to the desired hardness and which are utilized as fuels for the hydrazine nitroform oxidizer. The term "Fuel binder" as used throughout this invention not only includes the polymeric composition which is present in a major amount but also includes the minor amount of one or more curing agents, plasticizers, accelerators, etc., cannot be stated with precision.

Fuel binders containing substantial quantities of oxygen in the molecule are favored in order to maximize the amount of available gaseous products and to assist in the oxidation of the binder. Among the many favored oxygen-containing resins which can be used are the following: the polyamides, the polyesters, the polycarbonates, the polyacrylates, the polyepoxides as well as these resins modified by nitration and the like or these resins copolymerized with other resins or each other. While the polysulfides, polyalkylenes and other non-oxygen containing polymeric binders can be utilized for propellant compositions, their use is not particularly favored.

A group of fuel binders that are especially preferred because of their superior physical and combustion characteristics, are the polyesters, particularly the carboxyl-terminated carboranes or carboxyl-terminated polyalkadienes (such as polybutadiene) having a molecular weight ranging from 500 to 5,000 or more.

Where the preferred carboxyl-terminated carborane polyesters are used as fuel binders, the carborane polyester can be prepared among other ways by preparing the adduct of 1,4-butynediol and decarborane and esterfying the adduct with adipic acid under reaction conditions such as temperature, pressure and catalysts described in the esterification art. The reaction product is a liquid carboxy-terminated prepolymer heavily loaded with boron. This prepolymer is admixed with the other components of the composition and is cured at relatively elevated temperatures (about 50–150° F.) to form the final solid propellant composition.

Typical polycarboxylic acids which can be used as reactants in preparing the above-described carboxyl-terminated carborane polyesters include in addition to adipic acid, oxalic, sebacic, maleic, fumaric, and other acids as well as mixtures of these acids. Hydroxylated reactants in addition to 1,4-butynediol include among others the glycols such as: ethylene glycol, diethylene glycol, propylene glycol, polybutylene and polypropylene glycols, glycerols, sorbitols, castor oil, 1,2,6-hexane triol and the like as well as mixtures of these compounds and their analogues. The preparation of the preferred carborane prepolymers among others is described in copending S.N. 844,821 filed Oct. 2, 1959, now abandoned, in the United States Patent Office. The preferred carboxyl-terminated polybutadiene is a commercial polymer produced by Thiokol Chemical Corporation under the designation of "HC Polymer" and its preparation is described in S.N. 216,955 filed Aug. 15, 1962, now abandoned, in the United States Patent Office.

Whereas ordinarily the fuel binders contemplated are a single polymer, such as the polyacrylamides, the polysulfides, and the like, frequently it is advantageous to prepare mixtures of these resins or the resins modified by imparting additional functional groups to the resinous molecule. For example, a modified polyurethane resin can be prepared reacting a polyurethane with 1,2-ethane dithiol to result in a prepolymer which can be cured by the polysulfide type of cure. Another approach is to react a carboxyl-terminated polyester with a sulfide-terminated reactant such as 1,2-ethane dithiol. In this instance the resultant prepolymer is cured using the usual polysulfide curing conditions.

In all instances, the resin used as a fuel binder is cured according to the curing techniques well known to the particular resin art using the usual polymerization catalysts, curing agents or accelerators commonly used. For example, the polyesters are cured at temperatures ranging from 80–180° F. and above, using the usual curing agents such as polyimines, polyepoxides and the like. Both the polysulfides and the mercaptan-terminated polyurethanes are cured at temperatures ranging from 120–200° F. using peroxide curing agents such as benzoyl peroxide. Since the methods of preparing or modifying the various resins used as binders are not the novel feature of this invention, no attempt is made to describe these manipulations in detail. It shall suffice to say that the preparative methods and curing techniques are well-known procedures described in the technical literature, particularly in the "Plastics Application Series" published by Reinhold Publishing Corporation, New York City, N.Y.

(4) PROPELLANT ADJUVANTS

In addition to the curing agents, solvents, polymerization and vulcanization catalysts and the like which are included within the fuel binder content of the inventive propellant compositions, certain additives, ignition catalysts, conditioning or modifyng agents can often be advantageously added to the propellant compositions to alter or improve their physical and combustion characteristics. For convenience sake, these substances are herein generically referred to as propellant adjuvants and they can be present in the finished propellant composition in amounts from up to about 30 parts by weight down to 0 part by weight of the final propellant composition.

More commonly however, the adjuvants comprise from about 20 parts by weight or even less down to about 5 parts by weight of the gas generating composition. Among the many propellant adjuvants which can be used are included the following typical materials. Plasticizers such as the alkylphthalates and the like, and darkening agents such as carbon black or lamp black, ballistic agents such as potassium sulfate, hygroscopicity inhibitors such as dinitro-toluene and various combustion catalysts. The combustion catalysts are of diverse structure but generally are compounds containing oxygen. These catalysts can be inorganic or organic compounds. They include, among

many others, oxides, such as magnesium, titanium, calcium, molybdenum, and vanadium oxides and the like. Especially effective as combusion catalysts are the chromates and dichromates, generally with ammonium dichromate being a preferred catalyst. Organics such as nitrocellulose can also be effectively used.

A favored group of adjuvants are the finely divided high energy metals and non-metals such as aluminum, beryllium, boron, silicon and the like. These materials can be used untreated or they can be employed in the form of their polymer coated particles.

(5) PREFERRED PROPELLANT COMPOSITIONS

As indicated supra, for various reasons, certain individual components of the propellant compositions are preferred over others. Thus the preferred propellant compositions of this invention are made up of:

(1) from about 20–85% by weight of hydrazine nitroform oxidizer.
(2) from about 20–50% by weight of a carboxyl-terminated carborane polyester on carboxyl-terminated polyalkadiene fuel binder.
(3) from about 2–6% by weight of a liquid alkenyl succine anhydride such as dodecenyl succinic anhydride.
(4) from about 5–30% by weight of a propellant adjuvant particularly a polymer coated aluminum.

(6) COMPOUNDING THE INGREDIENTS

In preparing the solid gas-generating composition the following procedure among many others can be used.

The dried oxidizer (20–80 parts by weight) is reduced to a finely divided condition by grinding or some other means. From about 1 to 10 parts by weight of stabilizer and from about 15–35 parts by weight of combustible fuel binder, either prepared earlier from the reactants, or as the commercially available monomer or polymer is placed in a blending vessel equipped with an efficient spark-proof mixer and the fine particles of the oxidizer are added thereto.

Also ordinarily added at this time are 0–30 parts by weight of any propellant adjuvants that are required. During these additions efficient mixing is maintained until a homogenous mixture results. The total mixing time necessary for a uniform mixture varies according to the batch size but ordinarily at least 30 minutes of mixing is required with 90 minutes or more representing the extremes of mixing time. Finally the curing agent or agents where necessary are added and the mixing continued for an additional ½ to 1 hour. Then the uniformly blended, uncured propellant composition is cast into an engine casing and the composition is cured at the required temperature until the desired degree of hardness is obtained. The curing time and temperatures are dependent upon the particular resin used as a binder, and the batch size, among other things, and thus cannot be stated with precision. However, the following ranges of time and temperature are typical for curing a propellant compoistion containing the fuel binders described below:

Binder	Range of curing temperatures, (° F.)	Range of curing time (hours)
Preferred carboxylterminated carborane polyester.	50–70	96–120
	100–110	48–60
	120–150	24–96
Polyester	80–180	6–50
Polysulfide	120–200	6–70
Polybutadiene	120–135	96–110

In one embodiment of this invention the following propellant ingredients are blended in a conventional propellant blending mixer and a conventional vessel. A 76.5 parts by weight of commercially prepared hydrazine nitroform, 15.2 parts by weight of the carboxyl-terminated carborane polyester described previously, 1.6 parts by weight of hexyl succinic anhydride and 0.8 part by weight of magnesium oxide. The blended propellant mixture can be cured at temperatures up to 70° C. without significant gassing and was highly energetic upon ignition.

In another embodiment of this invention a 76.5 parts by weight portion of commercially available hydrazine nitroform, 15.2 parts by weight of the above described carboxyl-terminated carborane polyester, 1.6 parts by weight of dodecenyl succinic anhydride and 0.8 part by weight of magnesium oxide are blended together for 15 minutes until a homogenous propellant mixture results. The blended mixture can be cured up to 70° C. without significant gassing and was highly energetic upon ignition.

In still another embodiment of this invention a 76.5 parts by weight portion of commercially derived hydrazine nitroform, 15.2 parts by weight of the same carboxyl-terminated carborane polyester, 1.6 parts by weight of tricosenyl ($C_{23}H_{46}$) succinic anhydride and 0.8 part by weight of magnesium oxide are blended together for 20 minutes until a uniformly blended mixture is obtained. The blended mixture cured well at 70° C. and was highly energetic upon ignition.

In yet another embodiment of this invention a 76.8 parts by weight portion of commercially derived hydrazine nitroform, 15.3 parts by weight of the same carboxyl-terminated carborane polyester, 1.9 parts by weight of succinic anhydride and 1.1 parts by weight of magnesium oxide are blended together for 20 minutes until a uniformly blended mixture is obtained. The blended mixture cured well at 70° C. and was highly energetic upon ignition.

This invention is advantageous both in process and composition aspects. For example, the process of adding the dicarboxylic acid anhydride compositions to a hydrazine nitroform based propellant composition substantially prevents gassing and boiling over of the propellant formulation. In addition, the novel stability method produces a satisfactory cured solid propellant composition having high specific impulse. This is particularly advantageous where the binder utilized is the preferred carboxyl-terminated carbonane polyester type. These binders are especially desirable because they contain elemental boron, a high energy element. In the absence of stabilizer, the hydrazine nitroform propellants of the prior art overflow and gas during curing, leaving voids and cracks in the cured propellant and burning erratically.

In its composition aspect the invention disclosed a new series of highly energetic hydrazine based propellants heretofore not described in the literature. Further advantages of this invention in both its process and composition aspects will suggest themselves to those skilled in the art upon a perusal of this patent application. The examples which follow describe the preparation of representative formulations containing the preferred stabilizer dodecenyl succinic anhydride and the preferred binder, the carboxyl-terminated carbonane polyesters.

Example 1.—Preparation of a non-aluminized propellant containing hydrazine nitroform oxidizer and carborane polyester binder

Using the conventional blending techniques, equipment, and procedures described earlier, the following propellant ingredients are blended for 20 minutes.

Ingredients:	Percent by weight
Carboxyl-terminated carborane polyester	23.8
Dodecenyl succinic anhydride stabilizer	2.5
Magnesium oxide	1.25
Hydrazine nitroform	72.25

The homogenous blended mixture is cured at 120° F. for 24 hours. No gassing is observed and upon ignition, the cured solid propellant burned evenly and energetically. The even ignition as well as visual inspection of propellant samples indicates the absence of significant voids or cracks.

Using the same techniques and equipment and curing temperatures, the above ingredients without the use of dodecenyl succinic anhydride stabilizer are blended, cured

and ignited. Visual evidence of substantial gassing is observed and uneven burning of cured samples confirms this suspicion.

Example 2.—Preparation of a non-aluminized propellant containing hydrazine nitroform oxidizer and carborane polyester binder

Using the same procedure and equipment described in Example 1 the following propellant formulation is prepared:

Ingredients:	Percent by weight
Carboxyl-terminated carborane polyester	15.2
Dodecenyl succinic anhydride	1.6
Magnesium oxide	0.8
Aluminum coated with Parlon P [1]	5.9
Hydrazine nitroform	76.5

[1] A chlorinated polypropylene.

The homogenous blended mixture is cured at 120° F. for 24 hours. No gassing is observed during curing. Upon ignition even and energetic burning is observed confirming the absence of substantial gassing during the curing step.

Again an equivalent control is run eliminating the dodecenyl succinic anhydride stabilizer. Visible gassing is observed and erratic burning takes place upon ignition.

Example 3.—Preparation of a non-aluminized propellant containing hydrazine nitroform oxidizer and carborane polyester binder

Using the same procedure and equipment described in Example 1 the following propellant formulation is prepared:

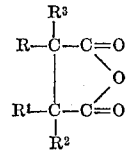
Ingredients:	Percent by weight
Carboxyl-terminated polybutadiene (HC Polymer)	12.3
Dodecenyl succinic anhydride stabilizer	2.4
Magnesium oxide	0.2
Aluminum coated with Parlon P	15.1
Hydrazine nitroform	70.0

Again the blended preparation is cured at 120° F. for about 24 hours. No visible gassing takes place and the energetic propellant formulation burns evenly.

A control run similar in all respects except that the stabilizer is omitted, is carried out. Visible gassing takes place. Ignition gives rise to an unevenly burning composition unsuitable for propellant applications. As indicated by the foregoing examples and embodiments, the scope of this invention is extensive. Furthermore, numerous modifications in conditions, reactants and techniques can be made without departing from the inventive concept which is defined by the accompanying claims.

What is claimed is:

1. A method of stabilizing hydrazine nitroform based propellant compositions comprising adding to said propellant compositions a stabilizing amount of the anhydrides of dicarboxylic acids of the formula:



wherein R, R^1, R^2 and R^3 are selected from the group consisting of hydrogen, alkyl, alkenyl, arylkyl and arylalkenyl radicals.

2. The method of claim 1 wherein the stabilizing amount of the anhydrides of dicarboxylic acid ranges from about 1 to 10% by weight of the propellant composition.

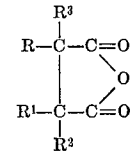
3. The method of claim 1 wherein the anhydride of dicarboxylic acid is a succinic acid anhydride.

4. The method of claim 1 wherein the anhydride of dicarboxylic acid is an alkyl succinic acid anhydride.

5. The method of claim 1 wherein the anhydride of dicarboxylic acid is an alkenyl succinic anhydride.

6. The method of claim 1 wherein the anhydride of dicarboxylic acid is an arylalkyl succinic anhydride.

7. The method of stabilizing a hydrazine nitroform based propellant composition comprising adding to said propellant composition a stabilizing amount of the anhydrides of dicarboxylic acids of the formula:



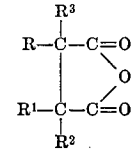
wherein R, R^1, R^2 and R^3 are selected from the group consisting of hydrogen, alkyl, alkenyl, arylalkyl and arylalkenyl radicals, said propellant composition being composed of from 20 to 85% by weight of hydrazine nitroform, 10 to 50% by weight of a combustive fuel binder and up to 30% by weight of propellant adjuvants.

8. The method of claim 7 wherein the stabilizing amount of the anhydrides of dicarboxylic acid ranges from about 1 to 10% by weight of the propellant composition.

9. The method of claim 7 wherein the combustible binder is a carboxyl-terminated carborane polyester.

10. The method of claim 7 wherein the combustible binder is a carboxyl-terminated polybutadiene.

11. A propellant composition composed of from about 20 to 85% by weight of hydrazine nitroform, from about 10 to 50% by weight of combustible fuel binder, up to 30% by weight of propellant adjuvants and a stabilizing amount of anhydrides of dicarboxylic acid stabilizers of the formula:



wherein R, R^1, R^2 and R^3 are selected from the group consisting of hydrogen, alkyl, alkenyl, arylalkyl and arylalkenyl radicals.

12. The composition of claim 11 wherein the stabilizing amount of the anhydrides of dicarboxylic acid ranges from about 1 to 10% by weight of the propellant composition.

13. The composition of claim 12 wherein the anhydride of dicarboxlic acid is an alkyl succinic anhydride.

14. The composition of claim 12 wherein the anhydride of dicarboxylic acid is an alkenyl succinic anhydride.

15. The composition of claim 12 wherein the anhydride of dicarboxylic acid is an arylalkenyl succinic anhydride.

16. The composition of claim 12 wherein the anhydride of dicarboxylic acid is dodecenyl succinic anhydride.

17. A propellant composition consisting of from about 20 to 85% by weight of hydrazine nitroform, from about 2 to 6% of dodecenyl succinic anhydride, from about 10 to 50% of a carboxyl-terminated carborane polyester and up to 30% weight of propellant adjuvants.

18. The composition of claim 17 wherein the propellant adjuvants are magnesium oxide and aluminum.

19. The composition of claim 18 wherein the aluminum is coated with a chlorinated polypropylene.

20. A propellant composition consisting of from about 20 to 85% by weight of hydrazine nitroform, from about 2 to 6% of dodecenyl succinic anhydride from about 10 to 50% of a carboxyl-terminated polybutadiene and up to 30% by weight of propellant adjuvants.

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U.S. Cl. X.R.

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