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2,992,908 SOLID ROCKET PROPELLANTS CONTAINING POLYLACTAMS

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24 Claims. (Cl. 52—5)

This invention relates to novel compositions of matter which are useful as solid rocket propellants and to the process of preparing same. More specifically this invention relates to compositions of matter comprising a lactam polymer and an alkali metal perchlorate oxidant, selected from the group sodium perchlorate and potassium perchlorate, and to the process of preparing same by the cast-polymerization of the lactam in the presence of the said oxidant.

Liquid compositions as the fuel-oxidant mixture for rockets present serious problems. The use of liquid propellants require considerable plumbing, valves, metering pumps and intricate controls to provide the means for effecting delivery of the fuel and oxidant to the combustion chamber in the proper ratio. The liquids employed are extremely corrosive and are also subject to loss. Therefore, rockets employing liquid propellant compositions are not reliable for long standing in ready-to-go condition. Furthermore, handling the corrosive liquids is a hazardous, time-consuming and cumbersome job, which precludes their use in tactical weapon systems in the field and aboard ships.

In contradistinction thereto the solid propellant motor is inherently very simple since the ratio and distribution of fuel, oxidant and additives are fixed when the solid propellant is prepared. Thus the solid propellant system requires no plumbing, valves, or controls and contains no mechanical moving parts which can go wrong. The solid propellant rocket also generally is characterized by relatively long storage life, ease in handling and high reliability, such that it is in constant readiness for instant use, whereby it is well adapted for tactical and strategic weapon systems in field use and aboard ships. A further advantage of the solid propellant rocket is that the relatively rigid propellant charge aids in the support of the chamber during handling and when in use such that a lighter-weight case can be employed, which saving in weight plus the elimination of much hardware required for a liquid propellant system provides a bigger pay-load.

The principal object of this invention is to provide an improved solid propellant composition. Another object of this invention is to provide an improved process for casting solid propellant compositions in rocket cases. Other objects and advantages of this invention will be apparent to those skilled in the art from the following disclosure.

It has now been found that the lactams, containing 5 to 7 members, i.e. from 4 to 6 carbon atoms, in the lactam ring, can be readily polymerized in the presence of major amounts of anhydrous sodium perchlorate and potassium perchlorate by relatively low-temperature, base-catalyzed, N,N-diacyl-initiated polymerization process whereby the novel propellant composition can be directly cast in a rocket motor case or other suitable container. Suitable lactam monomers which can be employed in the preparation of these novel solid rocket propellant compositions are for example, pyrrolidone, piperidone, and ϵ -caprolactam.

The preferred relatively low temperature, base-catalyzed, N,N-diacyl-initiated polymerization process is disclosed in the copending U.S. application Serial No. 627,

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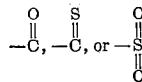
984, filed December 13, 1956, of which this application is a continuation-in-part.

Effective base catalysts are the alkali and alkaline earth metal catalysts, which are effective either in the metallic form or in the form of hydrides, borohydrides, oxides, hydroxides, carbonates, amides, etc. Lithium and sodium hydrides are particularly preferred catalysts in the composition of the present invention. The base catalyst is employed in an amount of from about 0.05 percent up to about 5 percent, and preferably from about 0.1 percent up to about 1 percent by weight of the lactam present in the composition.

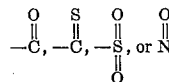
The N,N-diacyl compounds suitable as promoters can be selected from the class of compounds containing the essential active group:



wherein N is a tertiary nitrogen atom (i.e., has no hydrogen atoms attached thereto), A is an acyl radical selected from



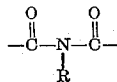
and B is an acyl radical selected from



and R is a third substituent of the same kind or general type as A or B; or a hydrocarbyl radical such as aryl, alkyl, aralkyl, alkaryl, cycloalkyl, etc.; or a heterocyclic radical such as pyridyl, quinolyl, etc.; or any of the aforementioned groups substituted with or containing additional radicals or groups such as carbonyl, N-substituted carbamyl, alkoxy, ether, sulfonyl, tertiary amino, etc.; or any other non-interfering groups, i.e., groups which will not preferentially react with the lactam or which will not otherwise interfere with the essential effective activity of the polymerization catalyst.

The substituents attached to the carbonyl, thiocarbonyl and sulfonyl radicals A and B are unlimited, provided they are free of interfering groups (e.g., primary amino groups or strong acid functions which will interfere with the alkali or alkaline metal catalysts). Examples of non-interfering groups are hydrogen atoms, as well as the hydrocarbyl and heterocyclic radicals mentioned in the preceding paragraph, including such radicals substituted with or containing polar-substituents such as tertiary amino, acylamido, N-substituted carbamido, ether, etc. The radicals A and B can be attached together to form a ring system (e.g., the cyclic imides described in greater detail below). Likewise, the radical A and the tertiary nitrogen atom can constitute a part of a ring system not including the radical B (e.g., the lactams described below).

A preferred class of materials having the aforementioned structure are N-substituted imides, i.e., compounds of the foregoing type having at least two acyl groups attached directly to the tertiary nitrogen atom. This group of compounds can be represented by the following structural formula:



A particularly effective class of N-substituted imides are the N-acyl lactams such as N-acetyl-2-pyrrolidone, N-acetyl- ϵ -caprolactam, N-benzoyl- ϵ -caprolactam, N-benzoyl- δ -valerolactam, N-ethylcarbamyl- ϵ -caprolactam, N-propionyl- ω -caprylactam, N-toloyl- ω -decanolactam, etc.

Another preferred class of N-substituted imides comprise the cyclic imides of dicarboxylic acids. Examples of this class are N-phenylsuccinimide, N-phenylmaleimide, N-methylsuccinimide, N-methylphthalimide, N-acetyl-tetrahydrophthalimide, N-benzoylsuccinimide, N-benzoylphthalimide, etc.

Another preferred class of N-substituted imides comprise those having a multiplicity of the essential N,N-diacyl tertiary nitrogen atom groups. This class includes compounds in which a portion of the group (for example, an acyl radical) is common to two or more of the essential polymerization promoting structures. Examples of this class are the N,N',N''-trimethylester of isocyanuric acid, N,N'-di(phenylcarbonyl)-N,N'-dimethylureas, ethylene disuccinimide, etc.

Examples of other N-substituted imides suitable for the above-described improved polymerization are N,N-diacylmethylamine, N,N-dibenzoylaniline, triacetamide, N-acetyl-N-formyl ethylamine, N-propionylsaccharin, etc.

Another general class of compounds useful for the polymerization process comprise the N-acyl sulfonamides containing no hydrogen atom on the sulfonamide nitrogen atom. Examples of this general class of materials are N-acetyl-N-ethyl-p-toluenesulfonamide, N-ethyl-N-lauroylethanesulfonamide, N,N-diacetyl-methanesulfonamide, N-(phenylsulfonyl)succinimide, N-methylsaccharin, N-acetylsaccharin, N-acetyl-N-methylbenzenesulfonamide and numerous other N-acyl sulfonamides.

Another class of suitable compounds for the polymerization process comprise the disulfonamides such as N,N-di(p-toluenesulfonyl)anilide, N,N-di(benzenesulfonyl)methylamine, and other N,N-dibenzenesulfonyl alkylamines, as well as the corresponding N,N-dialkane-sulfonylalkylamines such as N,N-di(methanesulfonyl)ethylamine, etc.

Another general type of effective promoter compounds comprise the N-nitrosoamides. Representative members of this class of compounds are N-nitroso-2-pyrrolidone, N-nitrososuccinimide, N,N-diacetylnitrosamine, N-nitroso-N-acetyl-propylamine, N-nitroso-N,N'-di-n-butylurea, N-methyl-N-nitrosourethane and other N-substituted N-nitroso-carbamates, etc.

Another general class of promoters for the polymerization process comprises the N-nitrososulfonamides, such as N-nitroso-N-methyl-benzenesulfonamide, N-nitroso-N-methyl-p-toluenesulfonamide, N-nitroso-N-ethyl-methanesulfonamide, N-nitroso-N-phenethyl-butanesulfonamide, etc.

As was indicated above, one or more of the acyl oxygen atoms of the various compounds described herein can be substituted with sulfur atoms to form the corresponding thioacyl compounds without destroying the effectiveness of such compounds as promoters for the polymerization of the lactams. Examples of such thio compounds are 1-acetyl-2-thiohydantoin and 3-butyl-5,5-dimethyl-2-thio-2,4-oxazolidinedione. Other suitable thio analogs of the foregoing acyl compounds are N-thiobenzoyl-2-pyrrolidone, N-thiopropionylmaleimide, N-phenyldithiosuccinimide, N-(n-octyl-carbamyl)-2-thiopyrrolidone, etc.

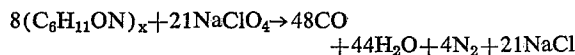
To preclude the presence of large inert groups being present in the above-described N,N-diacyl promoters it is preferred that the molecular weight of the compound does not exceed about 1000 and more preferably still does not exceed about 500.

The process can be carried out at temperatures up to 250° C. and preferably up to about 190° C. and more preferably between about 130° C. to about 170° C. for the polymerization of ε-caprolactam in the presence of major amounts of sodium and potassium perchlorate and down to about 35° C. for the lower molecular weight lactams, e.g., pyrrolidone.

The amount of N,N-diacyl promoter employed in the polymerization process can vary from about 0.01 to about 5 mole percent of the lactam monomer and will preferably vary from about 0.01 to about 2 mole percent, and more

preferably still from about 0.1 to 1 mole percent, the lower concentrations being used when a higher molecular weight polymer is desired.

In general the weight ratio of the alkali metal perchlorate to the poly lactam will vary from about 2.5:1 to about 3.5:1 depending on the alkali metal perchlorate selected, the particular poly lactam employed and the various additives which may be incorporated therein. For example, the weight ratio of the sodium perchlorate to polycaprolactam should preferably be about 2.84:1 to oxidize the polyamide according to the following equation



Similarly the preferred weight ratio of potassium perchlorate to polycaprolactam is 3.2:1.

Also the novel sodium and potassium perchlorate-poly lactam compositions of this invention can contain various other components finely dispersed therein such as the finely divided light metals and various hydrides thereof, e.g., beryllium, boron, magnesium, aluminum, magnesium hydride, aluminum hydride, the various solid hydrides of boron such as decaborane, alkylated decaboranes (ethyl alkylated decaborane), aluminum borohydride, and the like. Preferably the aforesaid materials should be sufficiently fine to all pass a standard 100-mesh screen, and more preferably should pass a 200-mesh screen.

These light metal and metal hydride high-energy additives should preferably not exceed about 25 weight percent of the total composition. Notwithstanding the relatively high-energy content per unit of weight of the aforesaid additives, the heavy combustion exhaust tends to lower the performance of the solid propellant composition such that it is often desirable to incorporate not more than from about 5 to about 10 weight percent of said additive, based on the total weight of the propellant composition.

Another class of additives which can be incorporated in the sodium or potassium perchlorate-poly lactam compositions are the relatively low molecular weight plasticizers, for example, the sulfonamides such as N-mono-substituted toluene sulfonamides, e.g., N-ethyl-p-toluenesulfonamide, N-ethyl-o-toluenesulfonamide and mixtures thereof disubstituted amides such as dimethyl formamide; and glycol ethers such as triethylene glycol dimethyl ether; butyrolactone; ethylene glycol; and the like. The plasticizer employed also functions as a fuel element in the composite solid propellant and the ratio of the sodium or potassium perchlorate is adjusted such that a proper balance is maintained between the oxidant and the fuel combinations to provide complete combustion. The amount of plasticizer employed can vary up to about 35 weight percent of the poly lactam present in the composition, but amounts of from about 15 to about 25 weight percent are generally preferred.

The sodium or potassium perchlorate-poly lactam compositions of this invention are useful as a solid propellant for rockets, for example short-range ballistic weapons, such as aircraft and artillery rockets. The aforesaid compositions are also useful for rocket assisted takeoff and as boosters and sustainers. These compositions are also useful as pyrotechnics. When confined the aforesaid compositions also are particularly valuable as explosives.

The following examples are illustrative of this invention.

Example 1

One part by weight of ε-caprolactam containing 0.01 part by weight of sodium hydride and 0.5 mole percent, based on the caprolactam, of N-acetyl caprolactam was heated to 160° C. and about 3 parts by weight of potassium perchlorate incorporated therein. The polymerization of the caprolactam took place very rapidly, the mixture being a solid mass after a total polymerization time of 10 minutes. The solid, uniformly mixed com-

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position was ignited with a flame and observed to burn with a vigorous, brilliant flame.

Example 2

A similar composition to that disclosed in Example 1 can also be prepared in the following manner. The monomeric material, ϵ -caprolactam, is introduced directly in a rocket motor case and 0.05 weight percent of sodium hydride and 1 mole percent of N-acetyl caprolactam, wherein the percent of the catalyst and promoter are based on the ϵ -caprolactam, are added thereto at a temperature of 80° C. Then 3.2 parts by weight, per part by weight of ϵ -caprolactam, of finely divided potassium perchlorate is added thereto and the oxidant and monomeric material are mixed to effect a substantially uniform composition. Then the mixture is heated to a temperature of about 160° C. to provide a solid composite rocket propellant.

Example 3

A further modification of the above examples can be effected in the following manner. The mixture of ϵ -caprolactam and 0.05 weight percent thereof of sodium hydride is heated to about 160° C. and introduced into the rocket motor case. Then 1 mole percent of N-acetyl caprolactam, based on the ϵ -caprolactam, is mixed therein and immediately thereafter 2.84 parts by weight, per part by weight of ϵ -caprolactam, of finely divided sodium perchlorate is added thereto and mixed uniformly therein. Thereafter the rocket motor case and contents are held at about 160° C. in an oven for about one-half hour to effect polymerization of the ϵ -caprolactam and provide a solid composite rocket propellant.

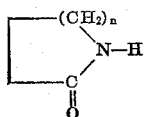
The polylactam must of course be polymerized to a sufficiently high molecular weight to provide a solid composite composition under temperatures to which the material may be exposed prior to firing. Accordingly, a molecular weight of at least about 10,000 should be effected in the cast-polymerization process of preparing composite compositions for solid rocket propellants.

When the sodium or potassium perchlorate-polylactam propellant composition is cast in a rocket casing the rocket motor case also can be lined with any suitable polymer composition and cured prior to loading with the fluid, unpolymerized propellant composition. Thereafter a core is placed in the fluid propellant composition, which core is subsequently removed after the mass has solidified, providing the desired internal cavity to effect proper radial burning of the propellant. These solid cast-polymerized sodium or potassium perchlorate-polylactam compositions burn vigorously and very uniformly when ignited, thereby providing an exceptionally good solid rocket propellant.

We claim:

1. A composition of matter consisting essentially of an intimate mixture of a polylactam, wherein the lactam monomer for the said polylactam contains from 4 to 6 carbon atoms in the lactam ring, and a member from the group consisting of sodium perchlorate, potassium perchlorate, and mixtures thereof, and the weight ratio of the said perchlorate to the said polylactam is from about 2.5:1 to about 3.5:1.

2. A composition of matter consisting essentially of a solid intimate mixture of a polylactam obtained by the polymerization of lactams defined by the structural formula:



wherein n is an integer from 3 to 5, inclusive, and an oxidant from a member of the group consisting of sodium perchlorate, potassium perchlorate, and mixtures thereof,

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and the weight ratio of the said perchlorate to the said polylactam is from about 2.5:1 to about 3.5:1.

3. The composition of matter of claim 2, wherein the polylactam is polycaprolactam.

4. The composition of matter of claim 3, wherein the oxidant is sodium perchlorate and the weight ratio is about 2.84.

5. The composition of matter of claim 3, wherein the oxidant is potassium perchlorate and the weight ratio is about 3.2.

6. The composition of matter of claim 2, wherein the polylactam is polypyrrolidone.

7. The composition of matter of claim 2, wherein the polylactam is polypiperidone.

8. A composition of matter consisting essentially of a solid intimate mixture of a polylactam, wherein the lactam monomer for the said polylactam contains from 4 to 6 carbon atoms in the lactam ring; from about 2.5:1 to about 3.5:1 parts by weight per part by weight of polylactam, of a member from the group consisting of sodium perchlorate, potassium perchlorate and mixtures thereof; and up to about 25 percent, by weight of the total composition, of a high-energy additive selected from the group consisting of beryllium, boron, magnesium, aluminum, magnesium hydride, aluminum hydride, aluminum borohydride, decaborane, alkylated decaborane, and mixtures thereof.

9. The process of preparing a solid rocket propellant comprising the polymerization of a lactam monomer containing from 4 to 6 carbon atoms in the lactam ring in the presence of from about 2.5 to 3.5 parts by weight, per part by weight of monomer of an anhydrous oxidant from a member of the group consisting of sodium perchlorate, potassium perchlorate and mixtures thereof, and effecting polymerization of said monomer by the presence of a base-catalyst in the amount of from about 0.05 to about 5 weight percent, based on the monomer, and from about 0.01 to about 5 mole percent, based on the monomer, of an N,N-diacyl promoter compound having a tertiary nitrogen atom and having at least two of the three N-substituents selected from the group consisting of carbonyl, thio-carbonyl, sulfonyl and nitroso radicals.

10. The process of claim 9, wherein the base-catalyst is present in the amount of from about 0.1 to about 1 weight percent, and the promoter is present in the amount of from about 0.1 to about 1 mole percent.

11. The process of claim 10, wherein the monomer is ϵ -caprolactam and the oxidant is sodium perchlorate.

12. The process of claim 11, wherein the polymerization process is carried out at a temperature below about 190° C.

13. The process of claim 12, wherein the base-catalyst is sodium hydride and the promoter is N-acetyl caprolactam.

14. The process of claim 12, wherein the sodium perchlorate is present in a weight ratio of about 2.84 times that of the caprolactam.

15. The process of claim 10, wherein the monomer is pyrrolidone and the oxidant is sodium perchlorate.

16. The process of claim 10, wherein the monomer is piperidone and the oxidant is sodium perchlorate.

17. The composition of matter of claim 1 having uniformly dispersed therein in a finely divided form up to about 25 percent, by weight of the total composition, of aluminum.

18. The composition of matter of claim 1 having uniformly dispersed therein in a finely divided form up to about 25 percent, by weight of the total composition, of boron.

19. The composition of matter of claim 1 having uniformly dispersed therein in a finely divided form up to about 25 percent, by weight of the total composition, of magnesium.

20. The composition of matter of claim 1 having uni-

formly dispersed therein in a finely divided form up to about 25 percent, by weight of the total composition, of magnesium hydride.

21. The process of preparing a solid rocket propellant composition comprising the process of claim 9, wherein up to 25 percent, by weight of the total composition, of finely divided aluminum is uniformly dispersed therein and maintained in a substantially uniform dispersion by mild agitation until the polylactam is advanced to a viscosity which retains the powdered aluminum in a substantially uniform dispersion and thereafter completing the polymerization of the monomer.

22. The process of preparing a solid rocket propellant composition comprising the process of claim 9, wherein up to 25 percent, by weight of the total composition, of finely divided boron is uniformly dispersed therein and maintained in a substantially uniform dispersion by mild agitation until the polylactam is advanced to a viscosity which retains the powdered boron in a substantially uniform dispersion and thereafter completing the polymerization of the monomer.

23. The process of preparing a solid rocket propellant composition comprising the process of claim 9, wherein up to 25 percent, by weight of the total composition, of finely divided magnesium is uniformly dispersed therein and maintained in a substantially uniform dispersion by mild agitation until the polylactam is advanced to a viscosity which retains the powdered magnesium in a sub-

stantially uniform dispersion and thereafter completing the polymerization of the monomer.

24. The process of preparing a solid rocket propellant composition comprising the process of claim 9, wherein up to 25 percent, by weight of the total composition, of finely divided magnesium hydride is uniformly dispersed therein and maintained in a substantially uniform dispersion by mild agitation until the polylactam is advanced to a viscosity which retains the powdered magnesium hydride in a substantially uniform dispersion and thereafter completing the polymerization of the monomer.

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