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SOLID COMPOSITE PROPELLANTS CONTAINING LITHIUM PERCHLORATE AND POLYAMIDE POLYMERS

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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 polyamide polymer, prepared by the condensation polymerization of a plurality of amine and carboxylic acid groups and lithium perchlorate and to the process of preparing same by blending.

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.

Conventional composite solid propellant compositions generally consist of an inorganic oxidant and a plastic binder, which also serves as the reductant fuel of the system. The aforesaid system is a heterogeneous composition wherein the burning rate and stability to detonation are dependent to some extent upon the particle size of the oxidant. Both of these properties are improved as the particle size of the oxidant is reduced, but milling to provide a finely divided oxidant is hazardous and periodic explosions are encountered.

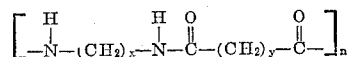
The principal object of this invention is to provide an improved solid propellant composition. Another object of this invention is to provide a novel solid propellant composition having a high specific impulse. A further object of this invention is to provide a novel solid pro-

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pellant composition which is homogeneous. A still further object of this invention is to provide a novel solid propellant composition characterized by improved stability to shock. 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 lithium perchlorate and the polyamide polymers, prepared by the condensation polymerization of a plurality of amine and carboxylic acid groups, are mutually soluble and the combination thereof is a homogeneous composition. The presence of the lithium perchlorate renders the polyamide polymer non-crystalline such that the polyamide polymer is in a rubbery, amorphous state, which is tougher than the crystalline product.

The polyamide polymers which can be employed in the preparation of the solid propellant compositions of this invention are those which are prepared by the condensation polymerization of, for example, a diamine and a dicarboxylic acid. These polymers can be illustrated by the structural formula:



wherein x and y are integers up to about 14 and preferably vary from about 4 to about 10, and n is an integer such that the molecular weight of the particular polymer can vary from about 7,000 up to about 75,000 and preferably from about 10,000 up to about 50,000. Thus, the polyamide must be of sufficiently high molecular weight that the composite composition with lithium perchlorate at normal storage conditions and ignition temperatures will be a solid, but not so high that the polyamide cannot be readily melt-blended with the lithium perchlorate, preferably at temperatures below about 250° C.

These polyamides are well known in the prior art and can be briefly illustrated as polyamides derived from the following diamines and dicarboxylic acids:

- 40 Hexamethylenediamine and adipic acid,
- Hexamethylenediamine and sebacic acid,
- Octomethylenediamine and adipic acid,
- Octamethylenediamine and sebacic acid,
- Decamethylenediamine and sebacic acid,
- 45 Tetramethylenediamine and suberic acid,
- Tetramethylenediamine and azelaic acid,
- Tetramethylenediamine and sebacic acid,
- Tetramethylenediamine and undecanedioic acid,
- 50 Pentamethylenediamine and glutaric acid,
- Pentamethylenediamine and pimelic acid,
- Pentamethylenediamine and suberic acid,

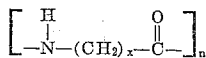
and the like. Also the diamine and dicarboxylic acid employed in the preparation of the polyamide can consist of more than a single diamine and/or dicarboxylic acid. Furthermore other than methylene units can be present in the polymer chain, as for example polyamides prepared by the condensation polymerization of

- 55 Hexamethylenediamine and β -methyl adipic acid,
- Hexamethylenediamine and 1,2-cyclohexanediacetic acid,
- Decamethylenediamine and p-phenylene diacetic acid,
- p-Xylylenediamine and sebacic acid,
- 3-methylhexamethylenediamine and adipic acid, and the like.

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The aforesaid class of polyamides can also be copolymerized with various amino acids for example copolymers of hexamethylenediamine and adipic acid with ϵ -amino caproic acid, and the like. Preferably such polyamide copolymers should contain at least about half of the polyamide units from the diamines and dicarboxylic acids.

The preferred amino acids which can also be employed to prepare the polyamides can be illustrated by the structural formula:

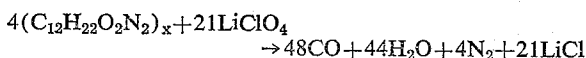


wherein x and n are as defined above. It will be understood that other than methylene units can be present in the polymer chain.

It has also been found that minor amounts of polyamides of relatively low molecular weight can be employed as resinous plasticizers for the higher molecular weight polyamides. Particularly suitable polyamides of this type are the condensation products of polymerized unsaturated fatty acids with aliphatic diamines, for example, dilinoleic acid with ethylene diamine, and the like. The higher molecular weight polyamides of the aforesaid type can also be employed as the sole plastic binder, so long as the softening point is sufficiently high to permit suitable ignition, as indicated hereinabove.

Since the lithium perchlorate and polyamide are mutually soluble they can be readily blended together at temperatures which are normally below the melting point of the polyamide composition. Preferably the two components are heated together at temperatures of from about 150° C. to about 250° C. with mild agitation in a suitable closed vessel. The blending operation is preferably carried out in an inert atmosphere, as for example nitrogen, and should be carried out with as little agitation as possible to preclude entrapment of gas in the composition. It is important to remove any occluded gas as for example by degassing under vacuum where necessary to provide a product of maximum density which will burn smoothly and uniformly. The polyamide, preferably in flake or chip form, can first be heated to the melting point and the lithium perchlorate added thereto as a solid or in a melted state, or the reverse order can be employed, or the two components can be heated together, to effect the homogeneous composition. The two components may also be blended together by means of an extruder or mill rolls operating in the aforesaid temperature range.

In general the weight ratio of the lithium perchlorate to the polyamide will vary from about 2:1 to about 4:1 depending on the particular polyamide employed and the various additives which may be incorporated therein. For example, the weight ratio of the lithium perchlorate to polyhexamethylene adipamide should preferably be about 2.5:1 to oxidize the polyamide according to the following equation:



where more energy may be desired by oxidation of the carbon monoxide to carbon dioxide, up to 33 moles of the lithium perchlorate can be employed, i.e., up to about 3.875 parts by weight of lithium perchlorate per part of the polyamide. It will be understood that the presence of other additives may alter the aforesaid weight ratios.

The composite system lithium perchlorate-polyhexamethylene adipamide for the weight ratio 2.47:1 was found to have a specific impulse of the order of about 250 sec. or higher at 1,000 p.s.i. chamber pressure. In addition to this desirable relatively high specific impulse the system is also extremely valuable in that it also possesses a high volume impulse value. The combination of these two desirable properties makes the composite solid rocket propellants of this invention particularly valuable in high performance applications.

Also the novel lithium perchlorate-polyamide compo-

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sitions 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 lithium perchlorate-polyamide compositions are the relatively low molecular weight plasticizers, for example, the sulfonamides such as N-monosubstituted toluenesulfonamides, 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; ethylene glycol; butyrolactone; and the like. The fairly polar plasticizers preferably should also be solvents for the lithium perchlorate such that the components of the system are mutually soluble or dispersible to effect a homogeneous solid composition. The presence of the plasticizer in the noncrystalline polyamide composite composition renders the composition more rubbery and provides a material improvement in the tensile elongation of the material. These composite compositions are characterized by their ability to provide a good seal between the solid propellant and the rocket motor case, which insures proper radial burning of the propellant without overheating the rocket motor case. The plasticizer employed also functions as a fuel element in the composite solid propellant and the ratio of the lithium 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 polyamide present in the composition, but amounts of from about 15 to about 25 weight percent are generally preferred.

The lithium perchlorate-polyamide compositions of this invention are useful as a solid propellant for rockets including short-range ballistic weapons, such as aircraft and artillery rockets, and long-range strategic missiles, wherein they may be the sole propellant or be employed in one or more stages of a multistage rocket system. The aforesaid compositions are also useful for rocket assisted takeoff and as boosters and sustainers. The lithium perchlorate-polyamide compositions of this invention can be drawn into fibers and cords which can be employed as a fuse, and the said compositions are also useful as pyrotechnics. When confined the aforesaid compositions also are particularly valuable as explosives.

The following example is illustrative of this invention:

Example 1

A mixture of 2.5 parts by weight of lithium perchlorate and 1 part by weight of a copolymer of hexamethylene adipamide and ϵ -aminocaproic acid was heated under nitrogen to 190° C. It was observed that the polymer softened, but no solution appeared to take place. The temperature was then raised to 225° C., whereat it was a fluid viscous mass which appeared to be homogeneous. The solid composite material burns vigorously and very uniformly when ignited.

A mixture of 2.5 parts by weight of lithium perchlorate and 1 part by weight of polyhexamethylene adipamide was heated under nitrogen to a temperature of 240° C. to effect a fluid homogeneous composition. The mixture was cooled to room temperature and found to burn vigorously and smoothly when ignited.

The blended lithium perchlorate-polyamide composition can also be readily extruded for use in relatively small-bore projectiles. When the solid propellant is produced by extrusion for insertion in small-bore rocket cases a small amount of the catalyzed-promoter system liquid polymer composition, described in our copending U.S. application Serial No. 719,503, filed March 6, 1958, can first be added to the cylinder case such that the insertion of the extruded mass will displace the liquid polymer forcing it to rise in the annular space between the extrusion mass and the cylinder wall whereby the inserted mass is securely bonded within the case. The liquid polymer also can be any other suitable polymer composition which can be readily cured at temperatures below about 200° C., as for example polyurethanes, epoxy resins, polysulfide rubbers and the like.

When the lithium perchlorate-polyamide 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 lithium perchlorate-polyamide 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 homogeneous lithium perchlorate-polyamide compositions burn vigorously and very uniformly when ignited, thereby providing an exceptionally good solid rocket propellant with relatively high specific impulse and high volume impulse.

We claim:

1. A composition of matter consisting essentially of a substantially homogeneous mixture of lithium perchlorate and a polyamide prepared by the condensation of polymerization of compounds selected from the group consisting of diamines, dicarboxylic acids and amino acids containing up to 14 carbon atoms in the chain linking the functional amine and carboxylic acid groups and the carbon chain linking said functional group contains only carbon and hydrogen atoms, and wherein the weight ratio of lithium perchlorate to said polyamide varies from about 2:1 to about 4:1.

2. 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.

3. The composition of matter of claim 1 having uniformly dispersed therein in a finely divided form a minor amount of boron.

4. The composition of matter of claim 1 having uniformly dispersed therein in a finely divided form a minor amount of magnesium.

5. 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 hydride.

6. A composition of matter consisting essentially of a homogeneous solid solution of lithium perchlorate and a polyamide prepared by the condensation polymerization of a diamine containing from 4 to 10 carbon atoms and a dicarboxylic acid containing 4 to 10 carbon atoms, exclusive of the carboxyl groups, and wherein the weight ratio of lithium perchlorate to said polyamide varies from about 2:1 to about 4:1.

7. The composition of matter of claim 6, having uniformly dispersed therein 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.

8. A composition of matter consisting essentially of a substantially homogeneous mixture of lithium perchlorate and polyhexamethylene adipamide in a weight ratio of from about 2:1 to about 4:1.

9. The composition of matter of claim 8, wherein the weight ratio is about 2.5:1.

10. A composition of matter consisting essentially of a substantially homogeneous mixture of lithium perchlorate and polyhexamethylene adipamide in a weight ratio of from about 2:1 to about 4:1, and uniformly dispersed therein 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.

11. The process of preparing a substantially homogeneous composition of lithium perchlorate and a polyamide, prepared by the condensation polymerization of compounds selected from the group consisting of diamines dicarboxylic acids and amino acids containing up to 14 carbon atoms in the chain linking the functional amine and carboxylic acid groups and the carbon chain linking said functional group contains only carbon and hydrogen atoms, comprising heating a mixture of lithium perchlorate and said polyamide in a weight ratio of from about 2:1 to about 4:1 to a temperature of up to about 250° C. until a homogeneous fluid mass is obtained and thereafter casting the fluid composition and allowing it to solidify.

12. The process of preparing a solid rocket propellant composition comprising the process of claim 11, wherein up to 25 percent, by weight of the total composition, of finely divided aluminum is uniformly dispersed in the homogeneous fluid mass prior to casting the fluid composition and allowing it to solidify.

13. The process of preparing a solid rocket propellant composition comprising the process of claim 11, wherein up to 25 percent, by weight of the total composition, of finely divided boron is uniformly dispersed in the homogeneous fluid mass prior to casting the fluid composition and allowing it to solidify.

14. The process of preparing a solid rocket propellant composition comprising the process of claim 11, wherein up to 25 percent, by weight of the total composition, of finely divided magnesium is uniformly dispersed in the homogeneous fluid mass prior to casting the fluid composition and allowing it to solidify.

15. The process of preparing a solid rocket propellant composition comprising the process of claim 11, wherein up to 25 percent, by weight of the total composition, of finely divided magnesium hydride is uniformly dispersed in the homogeneous fluid mass prior to casting the fluid composition and allowing it to solidify.

16. The process of preparing a substantially homogeneous composition of lithium perchlorate and a polyamide prepared by the condensation polymerization of a diamine containing from 4 to 10 carbon atoms and a dicarboxylic acid containing 4 to 10 carbon atoms, exclusive of the carboxyl groups comprising heating a mixture of lithium perchlorate and said polyamide in a weight ratio of from about 2:1 to about 4:1 to a temperature of from about 150° C. up to about 250° C. until a homogeneous fluid mass is obtained and thereafter casting the fluid composition and allowing it to solidify.

17. The process of claim 16, wherein the polyamide is polyhexamethylene adipamide and the temperature is from about 225° C. up to about 250° C.

18. The process of claim 17 wherein the lithium perchlorate is present in a weight ratio of about 2.5 times that of the polyhexamethylene adipamide.

19. The process of preparing a solid rocket propellant comprising the process of claim 11 wherein up to 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, is uniformly dispersed in a finely divided form in the homogeneous fluid mass and thereafter casting the mixture and allowing it to solidify.

20. The process of claim 19 wherein the polyamide is polyhexamethylene adipamide and the temperature is from about 225° C. up to about 250° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,479,470	Carr	Aug. 16, 1949
2,539,404	Crutchfield	Jan. 30, 1951
2,563,265	Parsons	Aug. 7, 1951
2,783,138	Parsons	Feb. 26, 1957
2,791,883	Moore et al.	May 14, 1957
2,855,372	Jenkins et al.	Oct. 7, 1958

OTHER REFERENCES

- Chem. and Eng. News, Jan. 6, 1958, pp. 79-81.
 Chem. and Eng. News, May 27, 1957, pp. 18-23.
 Arendale: Industrial and Eng. Chem., April 1956, pages 725-6.
 15 Deschere: "I.E.C.," vol. 49, No. 9, September 1957, pp. 1333-36.