SPHERICAL ANHYDROUS HYDRAZINE PERCHLORATE PELLETS AND PROPELLANTS PREPARED THEREFROM

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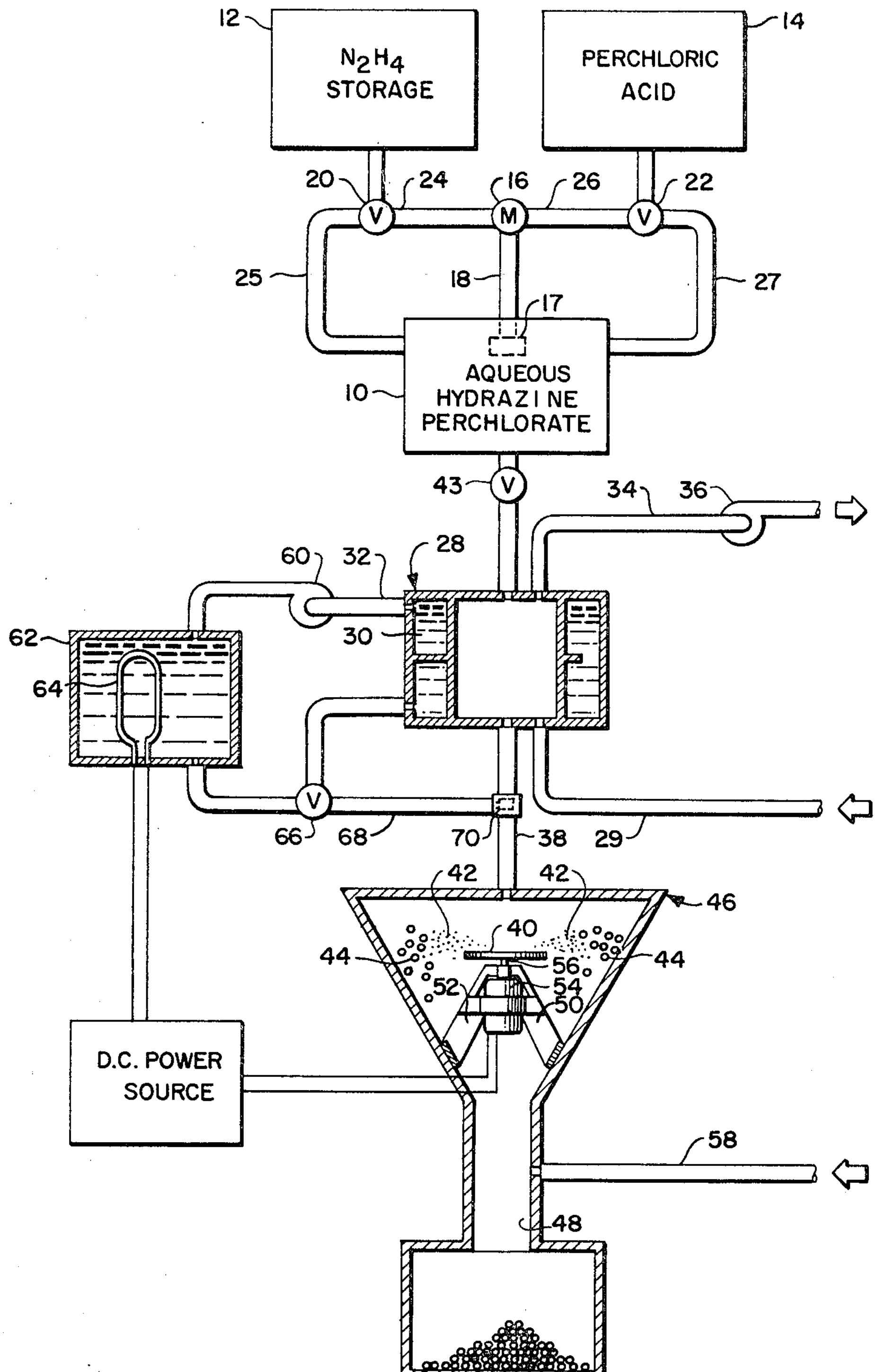

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SPHERICAL ANHYDROUS HYDRAZINE PERCHLORATE PELLETS AND PROPELLANTS PREPARED THEREFROM

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This invention relates to a method of preparing substantially spherical anhydrous hydrazine perchlorate. The invention further relates to an apparatus for use in preparing such hydrazine perchlorate. This invention also relates to the use of the novel hydrazine perchlorate spheres in the preparation of solid propellant formulations.

Hydrazine perchlorate is known as an oxidizer for use in solid propellant formulations. These solid propellant formulations have been used as the fuel for rocket engines. Previously, the hydrazine perchlorate used in propellant formulations was made of the desired size by grinding or crystallization. Hydrazine perchlorate prepared in this manner does not pack to a high density and thus it is not possible to obtain, by the use of such materials, a solid propellant containing the maximum solids content. The poor packing of the ground or crystallized hydrazine perchlorate is due to the jagged nature of the individual particles. These jagged shapes tend to create large void spaces between the individual hydrazine perchlorate particles. This results in the need for the use of excess binder material to hold the oxidizer together. This is undesirable in that the overall specific impulse of the propellant is reduced thereby. Therefore, it is desirable that the hydrazine perchlorate used in propellants be in spherical form. However, when spheres are formed from conventional hydrazine perchlorate, they tend to cake and to inhibit the cure of the binder upon incorporation in the propellant formulation.

It is an object of this invention to avoid the problems previously encountered with the use of ground or crystallized hydrazine perchlorate, or spheres of conventional hydrazine perchlorate.

It is a further object of this invention to prepare hydrazine perchlorate in the form of spheres which provide high bulk density and higher solids loading in the propellant.

It is also an object of this invention to prepare novel propellant formulations containing the new hydrazine perchlorate spheres which will cure to a tough, rubbery solid propellant without the need for large amounts of binder.

These and other objects of this invention will be apparent in the detailed description which follows:

According to this invention, substantially spherical hydrazine perchlorate propellants are continuously prepared by contacting a stream of molten anhydrous hydrazine perchlorate with the face of a rapidly spinning disk and collecting the solidified spheres at a distance from the periphery of the disk. The anhydrous hydrazine perchlorate is prepared by the dehydration of an aqueous solution of hydrazine perchlorate, said solution prior to dehydration containing about 20 percent to about 80 percent hydrazine perchlorate by weight and having a pH of from about 2 to about 6.

The process of this invention can be better understood by reference to the attached drawing, which is a schematic of the apparatus, preferably employed in continuously carrying out the process of this invention. The aqueous solution of hydrazine perchlorate containing from about 20 percent to about 80 percent hydrazine perchlorate by weight is continuously prepared in tank **10**.

The aqueous hydrazine perchlorate is made by continuously withdrawing neat hydrazine from tank **12** and perchloric acid, preferably 70 percent perchloric acid, from tank **14**. The pH within tank **10** is maintained within the prescribed range by the pH controller **16**. This device detects the pH within tank **10** by means of pH sensor **17** via line **18**, and in response thereto, continuously operates valves **20** and **22**, via lines **24** and **26**, and thus regulates the flow of hydrazine through line **25** and perchloric acid through line **27**.

The hydrazine perchlorate solution within tank **10** is continuously fed to evaporator **28**, the flow rate being regulated by valve **43**. The evaporator itself is preferably a continuous evaporator of the type made by the Vulcan Co. of Cincinnati, Ohio, and operates by passing a stream of a gas, such as air, countercurrent to the flow of wet hydrazine perchlorate. This gas is taken in through line **29** and the wet gas is expelled at the top of the evaporator which is connected through line **34** to vacuum pump **36**. The wet gas and dry hydrazine perchlorate are continuously withdrawn.

The dry hydrazine perchlorate leaves the evaporator at about 145°–150° C. in a molten condition. The necessary heat for the evaporator is provided by the heating jacket **30**, containing a heat transfer medium such as oil, introduced through line **32**. The oil is continuously recirculated by pump **60** through oil tank **62** containing heating element **64**. The rate at which the oil is recirculated is controlled by valve **66** which operates via line **68** in response to temperature sensor **70** located in the wall of line **38**. In this manner, the amount of heat furnished the evaporator may be controlled so as to maintain the temperature of the effluent hydrazine perchlorate within the above-mentioned desired range of about 145° C.–150° C.

The pressure within the evaporator is maintained by means of the vacuum pump **36**, at about atmospheric pressure. In this manner, substantially all the water is removed from the solution. The dehydrated hydrazine perchlorate thus obtained is then allowed to run via line **38**, which passes through the top closure of cone **46** (shown in vertical section) onto the spinning disk **40** at a rate of about 20 to 200 grams per minute, the rate being controlled by valve **43**.

The molten hydrazine perchlorate can be introduced at the center or off center of the spinning disk. The molten hydrazine perchlorate spreads out into a thin film on the disk and is thrown off the periphery in the form of small drops, **42**. The small drops form into spheres **44** due to surface tension. The spherical drops of hydrazine perchlorate cool and freeze within a short distance from the disk and are easily collected by means of the surrounding collecting cone **46**. As can be seen in the drawing, the spheres formed in the cone drop to the bottom and may be withdrawn through the opening **48**. The spinning disk is supported within the cone by braces **50** and **52**, and is powered by a variable speed D.C. motor **54**, mounted on shaft **56**.

The cone is filled with an inert dry gas such as dry nitrogen or dry argon, through line **58**. Normally, the dry gas within the cone is kept at a temperature of from about 0° C. to about room temperature.

The exact dimensions of the spinning disk and the surrounding cone are not critical. However, normally the cone should be sufficiently larger than the disk so as to permit the molten spheres which are flung off of the disk to harden prior to contact with the wall of the cone. Preferably, the spinning disk is from about 2 inches to about 10 inches in diameter and the cone is from about 4 feet to about 25 feet in diameter along the plane of the disk. Thus, the ratio of the diameter of the disk to the diameter of the cone along the plane of the disk is from about 1 to 24 to about 1 to 30.

The spinning disk itself can optionally be preheated by a heating element (not shown) located beneath the disk to the temperature of the molten hydrazine perchlorate so as to prevent freezing of the hydrazine perchlorate on the disk. Once the process is in operation, no further heating of the disk is normally necessary since the continous flow of hydrazine perchlorate onto the disk will maintain the disk temperature at that of the hydrazine perchlorate. Preferably, the disk has a very smooth surface, and is made of stainless steel.

The speed of rotation of the disk may be varied over a wide range. In general, the higher the r.p.m. of the disk, the smaller the hydrazine perchlorate particles produced. However, particle size is also a function of the disk size. Thus, at a given r.p.m., the larger the disk, the smaller the hydrazine perchlorate particle size. Normally, when employing a disk of from 2 inches to about 10 inches in diameter, the r.p.m. is varied from about 1000 r.p.m. to about 15,000 r.p.m.

While the foregoing description sets forth a method for continuously producing the hydrazine perchlorate spheres, it should be understood that the process of this invention can also be carried out batchwise. Thus, the perchloric acid and hydrazine can be manually mixed, and the pH adjusted to the proper range. The aqueous hydrazine perchlorate can then be placed in glassware such as a separatory funnel and heated to drive off the water. The molten hydrazine perchlorate can then be run out the bottom of the funnel onto the spinning disk which is within a collecting vessel. This batchwise procedure is particularly suitable where it is desired to prepare relatively small amounts of the hydrazine perchlorate spheres.

The hydrazine perchlorate spheres formed in accordance with the practice of this invention will normally vary in average diameter from about 10 microns to about 500 microns, depending upon the disk size and the r.p.m. of the disk, contain less than 0.1 percent by weight of water, and normally within the range of 0.1 percent to 0.005 percent. The spheres when dissolved in water in an amount of from about 20 percent to about 80 percent by weight of the total solution have a pH of about 2 to about 6.

The following examples are presented for purposes of illustration only and should not be regarded as limitative of the scope of the invention in any way. In the following examples, the percentages and parts are by weight unless otherwise indicated.

EXAMPLE I

Thirty-two grams of anhydrous hydrazine were added to 60 ml. of water. The resulting solution was titrated with 70 percent perchloric acid to a pH of 3.5 at 40° C. The solution of hydrazine perchlorate was then transferred to the jacketed receiver. The solution was then heated by circulating warm oil through the heating jacket to a temperature of 150° C. A vacuum was gradually applied until a pressure of 100 microns was obtained within the receiver. After several minutes at this temperature and pressure, molten dehydrated hydrazine perchlorate was obtained. This hydrazine perchlorate was then added through the opening at the bottom of the receiver to the center of the 3″ stainless steel disk at a rate of 100 grams per minute. The disk, which was preheated to a temperature of 150° C. was operated at 3300 r.p.m. and was at the center of a cone which was 6′ in diameter along the plane of the disk. The spherical hydrazine perchlorate which was withdrawn continuously from the bottom of the cone contained 0.02 percent water by weight. Microscopic analysis of the product showed all of the hydrazine perchlorate to be substantially spherical. The Tyler screen analysis of this spherical hydrazine perchlorate was as follows:

2.7 percent by weight larger than 48 Tyler
58.8 percent smaller than 48 Tyler, but larger than 100 Tyler
36.3 percent smaller than 100 Tyler, but larger than 200 Tyler
2.2 percent smaller than 200 Tyler, but larger than 325 Tyler
trace—smaller than 325 Tyler

When the foregoing experiment was repeated operating the spherical disk at 10,500 r.p.m., the screen analysis of the spherical hydrazine perchlorate produced was as follows:

None larger than 48 Tyler
0.4 percent smaller than 48 Tyler, but larger than 100 Tyler
22.1 percent smaller than 100 Tyler, but larger than 200 Tyler
33.8 percent smaller than 200 Tyler, but larger than 225 Tyler
43.7 percent smaller than 325 Tyler

When the above experiment was repeated at 3300 r.p.m. with the pH prior to dehydration being adjusted to a pH of 1, the spherical hydrazine perchlorate produced was found to cake badly. The clumps of hydrazine perchlorate were unsatisfactory for the preparation of a highly loaded solid propellant.

When the foregoing experiment was repeated at a pH prior to dehydration of pH 7, hydrazine perchlorate did not form spheres. Rather, the hydrazine perchlorate formed uneven clumps which upon incorporation in a polyurethane binder comprised of polypropylene glycol, glycerol monoricinoleate, dioctyl azelate and tolylene diisocyanate in the equivalent proportions, respectively, 60/40/20/107, resulted in a formulation which could not be completely cured even after retention at 130° F. for several days.

The spherical hydrazine perchlorate prepared in the foregoing manner can be used directly as the oxidizer in the preparation of solid propellants. The binder materials used to prepare such propellants can be any of the polymers disclosed in assignee's copending U.S. applications, Ser. No. 33,054 and Ser. No. 33,055, filed May 31, 1960. Thus, propellants containing well-known binders such as, for example, polyurethane, nitropolyurethane, polyesteracrylate, rubber (butyl, polysulfide), etc., are all within the scope of this invention.

The polyurethane binders used in this invention are prepared by reacting a compound having two or more active hydrogen containing groups as determined by the Zerewitinoff method, and capable of polymerizing with an isocyanate; with an organic compound having as the sole reacting groups, two or more isocyanate or isothiocyanate groups. The compound having the active hydrogen containing groups is preferably an organic compound having as its sole reacting groups, hydroxyl or thiol groups.

It will be apparent that, where there are more than two active hydrogen, isocyanate, or isothiocyanate groups present in any of the polyurethane reactants, the molecular structure of the resulting polyurethane binder will be at least to a certain extent of a cross-linked nature. The cross-linking is accomplished when all three functional groups of a sufficient number of the trifunctional molecules undergo the urethane reaction with other groups present in the mixture thus resulting in a product having a "three-dimensional" molecular structure.

Where bifunctional reactants, such as dihydroxy compounds and diisocyanates, are employed to produce the polyurethane binders, it is necessary to also employ a "cross-linking" agent to assure a product having the cross-linked structure essential to this invention. Compounds suitable as cross-linking agents for the polyurethane binders are those organic compounds having as the sole reacting groups three or more groups polymerizable with active hydrogen containing groups or isocyanate groups.

The isocyanate starting materials for the polyurethane binders are preferably diisocyanates but not necessarily so since, as explained above, other polyisocyanates (such as triisocyanates) or polyisothiocyanates may be employed within the scope of the invention if desired.

The preferred diisocyanate compounds can be saturated or unsaturated; aliphatic or aromatic; open or closed chain, and, if the latter, monocyclic or polycyclic; and substituted or not by groups substantially unreactive with isocyanate or hydroxyl groups. Illustrative diisocyanate compounds particularly suitable as reactants for the preparation of polyurethane binders are propylene-1,2-diisocyanate; tetramethylene diisocyanate; cyclohexylene-1,3-diisocyanate; m-phenylene diisocyanate; o-phenylene diisocyanate; p-phenylene diisocyanate; diphenylene-4,4'-diisocyanate; 2,4-tolylene diisocyanate; 2,6-tolylene diisocyanate; and 4,4'-diphenylmethane diisocyanate.

The preferred hydroxy starting materials for the polyurethane binders are dihydroxy compounds having the general formula: HO—R—OH; where R is a divalent organic radical. The hydroxy groups on the above compounds can be of any type suitable for the urethane reaction with isocyanate groups such as, for example, alcohol or phenolic hydroxy groups. Typical dihydroxy compounds suitable as reactants for the polyurethane binders are ethylene glycol and xylylene-1,3-diol.

Other dihydroxy compounds suitable in making polyurethane binders are hydroxy-terminated polyesters such as those obtained from the reaction of a dihydric alcohol such as ethylene glycol, with a dicarboxylic acid such as succinic acid. The polyesters most suitable for making polyurethane binders are those having a molecular weight from about 1000 to about 2500.

In addition to the polyesters, polyethers such as polyethylene ether glycols, polypropylene ether glycols, other polyalkylene ether glycols, the reaction product of 10 to 200 moles of the lower alkylene oxides such as ethylene or propylene oxide with one mole of glycerin or trimethylol propane, and mixtures or copolymers thereof having molecular weight of from about 400 to about 10,000 can be utilized as dihydroxy reactants of the preparation of polyurethane binders.

Examples of compounds which are particularly suitable as polyurethane cross-linking agents are glycerol monoricinoleate; glycerol triricinoleate, 1,2,6-hexanetriol; methylene bis (orthochloroaniline); sorbitol, monohydroxyethyl trihydroxypropyl ethylenediamine; polyaryl polyisocyanates; pentaerythritol-propylene oxide adduct; N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine; triethanolamine; trimethylolpropane; and triisocyanates, such as toluene-2,4,6-triisocyanate.

It is within the scope of the invention to employ any other solid propellant binder in the propellants containing spherical hydrazine perchlorate as the oxidizer. For example, resinous binders such as rubbers, polysulfides, rubber-polysulfide mixtures, other combustible polymeric organic materials, etc., are all suitable for this purpose. Examples of combustible polymeric organic materials suitable as propellant binders are phenol-aldehyde resins,

Examples of rubber binders which can be employed within the scope of this invention are polyisobutylene, butyl rubber, butadiene-styrene copolymers such as Buna-S, a butadiene-acrylonitrile copolymer such as Buna-N, highly polymerized vinyl alcohols in a plasticized state such as polyvinyl alcohol and chloroprene polymers such as Neoprene. The polysulfides suitable as solid propellant binders are exemplified by polyalkylene sulfides such as that resulting from the condensation of ethylene dichloride and sodium tetrasulfide. A more complete description of rubber and polysulfide propellant binders can be found in assignee's U.S. Pat. No. 3,012,866, issued Dec. 12, 1961.

The so-called polyester resins suitable for use as solid propellant binders are formed by reacting a polyhydric alcohol with a polycarboxylic acid and copolymerizing therewith a monomeric olefinic component such as vinyl, allyl, or other olefin compatible with the resin. To permit heteropolymerization between the polyester and olefin components, the polyesters are provided with some unsaturation through the incorporation therein of unsaturated polycarboxylic acid or anhydride and/or unsaturated polyhydric alcohol.

The polyester resins suitable as propellant binders and their methods of preparation are more fully disclosed in assignee's U.S. Pat. No. 3,031,288, issued Apr. 24, 1962.

Polyurethane resins containing unreduced oxygen are suitable binders for the propellants of this invention. Such binders can be prepared by condensing nitro-containing isocyanates and nitro-containing alcohols, as more fully disclosed in assignee's copending U.S. patent application, Ser. No. 728,491, filed Apr. 14, 1958.

Still other binder materials useful in the practice of this invention are the low molecular weight isoolefin-polyolefin copolymers disclosed in assignee's copending U.S. patent application Ser. No. 202,351, filed June 8, 1962; and the curable adducts prepared by reaction of polyaliphatic or polyether polymers with organic diacid anhydrides, disclosed in assignee's copending U.S. patent application, Ser. No. 241,058, filed Nov. 29, 1962.

Burning rate modifiers and other additives such as anti-oxidants, plasticizers, resonance suppressors, combustion additives, wetting agents, anti-foaming agents, etc., can be employed, if desired, in the formulation of our novel propellants. In this connection, copper chromite and finely divided carbon black, when utilized in small quantities (comprising preferably not greater than 1 percent, of the total propellant weight) are useful for increasing the burning rate of the propellant. Certain well-known wetting agents, such as lecithin, can be useful processing aids in the preparation of the novel propellants. Various additives other than those specifically mentioned can be employed, in minor amounts, within the scope of the invention. For example, phenyl betanaphthylamine can be utilized in very small quantities as an antioxidant. Likewise, powdered metals and metal oxides such as aluminum and aluminum oxide, may be added.

There are many ways of processing the various ingredients within the scope of this invention in the formulation of propellants therefrom, and these procedures may be readily determined by those skilled in the art, depending on the precise binder, plasticizer, etc. selected, and size of the batch to be prepared.

One technique which is quite satisfactory for the preparation of polyurethane propellants comprises addition of the wetting agent or agents, along with the plasticizer, to the diol and cross-linker in the mixer; addition of the burning rate modifiers (such as copper chromite and carbon black) during addition of the hydrazine perchlorate oxidizer; and addition of the curing catalyst (such as ferric acetylacetonate) along with addition of the diisocyanate. Modifications of the above methods of introducing the additives, such as, for example, addition of the wetting agents to the diol prior to introduction into the mixer, are varied and many.

After the propellant batch has been mixed to substantial uniformity, it is cast, extruded, or compression-formed to the desired shape and cured at a temperature preferably within the range from about 40° F. to about 180° F. The propellant mixture can be cast directly into a rocket chamber lined with an inert liner material, and polymerized (cured) therein if this procedure appears to be desirable.

The propellant binder is preferably employed in a proportion within the range from about 5 to about 55 percent based on the total weight of propellant, and the spherical hydrazine perchlorate in an amount within the range from about 95 to about 45 percent by weight.

As is pointed out above, the spherical hydrazine perchlorate prepared by the process of this invention can be used directly in the preparation of solid propellant formulations. However, it has been found that optimum solid loading with the spherical hydrazine perchlorate is obtained by employing a bimodal mixture of the spherical hydrazine perchlorate. Such a bimodal mixture is obtained by screening the hydrazine perchlorate spheres produced in the above manner to obtain one fraction which is, for example, of about 10 microns in diameter and another fraction which is, for example, about 100 microns in diameter, and then mixing the two fractions. Thus it has been found that the solids loading is further increased if the bimodal mixture consists of hydrazine perchlorate spheres, the ratio of diameter of the large spheres to the diameter of the small spheres being on the order of 10 to 1; i.e., 100 microns and 10 microns, 400 microns and 40 microns, etc. Usually the mixture is 50 to 90 percent by weight of the larger-sized fraction if the optimum oxidizer density in the propellant is to be achieved.

The following example illustrates the improved solids loading obtained using spherical hydrazine perchlorate rather than the ground hydrazine perchlorate of the prior art.

EXAMPLE II

A propellant was prepared by adding to a mechanical mixer 70 parts of a bimodal mixture of spherical hydrazine perchlorate prepared in the manner described above (the larger sized fraction being smaller than 48 Tyler, but larger than 100 Tyler, and being 75 percent by weight of the oxidizer mixture and the balance being a smaller sized fraction which had a diameter less than 325 Tyler). To the mixer were then added 10 parts of a binder consisting of 6 parts of isododecyl pelargonate as a plasticizer, and 4 parts by weight of a polymer (prepared by reacting one mole of polypropylene ether glycol having a molecular weight of about 1100 with about 2 moles of tetrachlorophthalic anhydride). Then 20 parts of aluminum, as a combustion additive, and 0.9 part of tris (methyl aziridinyl) phosphine oxide as a cross-linking agent were added. The ingredients were found to mix readily, and the resulting blend was easily castable, i.e., pourable into the motor casing. The cast propellant cured to a good rubbery elastomer at room temperature in three hours.

The foregoing example is repeated, using a bimodal mixture of 75 percent by weight of a ground hydrazine perchlorate which is smaller than 48 Tyler but larger than 100 Tyler, and 25 percent by weight of ground hydrazine perchlorate which is smaller than 325 Tyler, as the oxidizer. The resultant formulation became so thick that thorough mixing could not be achieved, nor could the thickened mass be cast into a motor casing because the amount of binder material was insufficient to form a uniform, liquid mixture.

The foregoing experiment illustrates the increased solid loading obtainable using the spherical hydrazine perchlorate prepared in accordance with the instant invention.

The following are other solid propellant formulations employing the spherical hydrazine perchlorate of this invention.

EXAMPLE III

Ingredients:	Weight percent
Spherical hydrazine perchlorate (prepared in accordance with Example I)	76.00
Polypropylene glycol (molecular weight 1800–1900)	16.67
2,4-toluene diisocyanate	2.75
Glycerol monoricinoleate	2.05
Di-2-ethylhexyl azelate	2.39
Lecithin	0.05
Ferric acetylacetonate	0.09
Total	100.00

The above composition is cured to a rubbery solid propellant by curing for two days at 130° F.

EXAMPLE IV

Ingredients:	Weight percent
Spherical hydrazine perchlorate (prepared in accordance with Example I)	55.00
Powdered aluminum	20.00
Liquid isobutylene-isoprene copolymer (prepared in accordance with copending application Ser. No. 202,351)	15.60
Polyisobutylene plasticizer	3.20
Dinitrosobenzene (curing agent)	6.20
Total	100.00

The foregoing composition is cured to a rubbery solid propellant by curing for about 5 days at 150° F. When the hydrazine perchlorate spheres of this invention are used as the oxidizer ingredient in any of the propellant formulations disclosed in assignee's copending U.S. patent application Ser. No. 829,180, filed July 20, 1959, satisfactory results are obtained.

I claim:

1. A method for the continuous preparation of substantially spherical anhydrous hydrazine perchlorine pellets which comprises contacting a stream of molten hydrazine perchlorate with the face of a rapidly spinning disk and collecting the solidified spheres at a distance from the periphery of the disk, said anhydrous hydrazine perchlorate having been obtained by the dehydration of an aqueous solution of hydrazine perchlorate, said solution prior to dehydration containing 20% to 80% hydrazine perchlorate by weight, and having a pH of from about 2 to about 6.

2. A method for the continuous preparation of substantially spherical anhydrous hydrazine perchlorate pellets which comprises contacting a stream of molten anhydrous hydrazine perchlorate with the face of a rapidly spinning disk and collecting the solidified spheres at a distance from the periphery of the disk, said anhydrous hydrazine perchlorate having been obtained by the dehydration of an aqueous solution of hydrazine perchlorate, said solution prior to dehydration containing 20% to 80% hydrazine perchlorate by weight and having a pH of about 3.5.

3. A method for the continuous preparation of substantially spherical anhydrous hydrazine perchlorate pellets which comprises contacting a stream of molten anhydrous hydrazine perchlorate with the face of a rapidly spinning disk and collecting the solidified spheres at a distance from the periphery of the disk, said anhydrous hydrazine perchlorate having been obtained by the dehydration of an aqueous solution of hydrazine perchlorate, said solution prior to dehydration containing about

55% hydrazine perchlorate by weight and having a pH of about 3.5.

4. A method for the continuous preparation of substantially spherical anhydrous hydrazine perchlorate pellets which are from about 10 microns to about 500 microns in average diameter and which contain less than 0.1% by weight of water which comprises contacting a stream of molten anhydrous hydrazine perchlorate with the face of a rapidly spinning disk and collecting the solidified spheres at a distance from the periphery of the disk, said anhydrous hydrazine perchlorate having been obtained by the dehydration of an aqueous solution of hydrazine perchlorate, said solution prior to dehydration containing 20% to 80% hydrazine perchlorate by weight and having a pH of from about 2 to about 6.

5. A method for the continuous preparation of substantially spherical anhydrous hydrazine perchlorate pellets which comprises contacting a stream of molten anhydrous hydrazine perchlorate with the face of a rapidly spinning disk, said disk being approximately the same temperature as the molten anhydrous hydrazine perchlorate, and collecting the solidified spheres at a distance from the periphery of the disk, said anhydrous hydrazine perchlorate having been obtained by the dehydration of an aqueous solution of hydrazine perchlorate, said solution prior to dehydration containing 20% to 80% hydrazine perchlorate by weight and having a pH of from about 2 to about 6.

6. A method for the continuous preparation of substantially spherical anhydrous hydrazine perchlorate pellets which comprises contacting a stream of molten anhydrous hydrazine perchlorate with the face of a stainless steel disk which is rotating at a rate of from about 1000 to about 15,000 r.p.m., and collecting the solidified spheres at a distance from the periphery of the disk, said anhydrous hydrazine perchlorate having been obtained by the dehydration of an aqueous solution of hydrazine perchlorate, said solution prior to dehydration containing 20% to 80% hydrazine perchlorate by weight and having a pH of from about 2 to about 6.

7. A method for the continuous preparation of substantially spherical anhydrous hydrazine perchlorate pellets which comprises contacting molten anhydrous hydrazine perchlorate at the rate of about 100 grams per minute, with the face of a rapidly spinning disk and collecting the solidified spheres at a distance from the periphery of said disk, said anhydrous hydrazine perchlorate having been obtained by the dehydration of an aqueous solution of hydrazine perchlorate, said solution containing prior to dehydration 20% to 80% hydrazine perchlorate by weight and having a pH of from about 2 to about 6.

8. A method for the continuous preparation of substantially spherical anhydrous hydrazine perchlorate pellets having an average diameter of from about 10 microns to about 500 microns which comprises contacting a stream of molten anhydrous hydrazine perchlorate at a rate of about 100 grams per minute with the face of a 3" stainless steel disk, said disk rotating at a rate of from about 1,000 r.p.m. to about 15,000 r.p.m. and collecting the solidified spheres at a distance from the periphery of the disk, said anhydrous hydrazine perchlorate having been obtained by dehydration of an aqueous solution of hydrazine perchlorate, said solution prior to dehydration containing 20% to about 80% hydrazine perchlorate by weight and having a pH of from about 2 to about 6.

9. A method for the continuous preparation of substantially spherical anhydrous hydrazine perchlorate pellets having an average diameter of from 10 microns to about 500 microns, and containing less than 0.01 percent water by weight, which comprises contacting a stream of molten anhydrous hydrazine perchlorate at a rate of about 100 grams per minute with the face of a 3 inch stainless disk which is rotating at a rate of from about 1,000 r.p.m. to about 15,000 r.p.m. and collecting the solidified spheres at a distance from the periphery of the disk, said anhydrous hydrazine perchlorate having been obtained by the dehydration of an aqueous solution of hydrazine perchlorate, said solution prior to dehydration containing 20 percent to 80 percent hydrazine perchlorate by weight and having a pH of from about 2 to about 6.

10. A method for the continuous preparation of substantially spherical anhydrous hydrazine perchlorate pellets which comprises contacting a stream of molten hydrazine perchlorate, said stream being at a temperature of about 150° C., with the face of a rapidly spinning disk, said disk being at a temperature substantially the same as that of the molten anhydrous hydrazine perchlorate, and collecting solidified spheres at a distance from the periphery of the disk, said anhydrous hydrazine perchlorate having been obtained by the dehydration of an aqueous solution of hydrazine perchlorate, said solution prior to dehydration containing 20% to 80% hydrazine perchlorate by weight and having a pH of from about 2 to about 6.

11. Substantially spherical anhydrous hydrazine perchlorate having an average diameter of from about 10 microns to about 500 microns, and containing less than about 0.1 percent by weight of water, said spheres when dissolved in water in an amount from about 20% to about 80% by weight of the total solution having a pH of from about 2 to about 6.

12. Substantially spherical anhydrous hydrazine perchlorate having an average diameter of from about 10 microns to about 500 microns, and containing less than about 0.1 percent by weight of water, said spheres when dissolved in water in an amount from about 20% to about 80% by weight of the total solution having a pH of about 3.5.

13. A solid propellant composition which comprises a cured intimate mixture of an oxidizer comprising substantially spherical anhydrous hydrazine perchlorate having a diameter of from about 10 microns to about 500 microns containing less than about 0.1 percent by weight of water, said spheres when dissolved in water in an amount from about 20% to about 80% by weight of the total solution having a pH of from about 2 to about 6, and a resin binder.

14. A solid propellant composition which comprises a cured intimate mixture of an oxidizer comprising substantially spherical anhydrous hydrazine perchlorate having an average diameter of from about 10 microns to about 500 microns, and containing less than about 0.1 percent by weight of water, said spheres when dissolved in water in an amount from about 20% to about 80% by weight of the total solution having a pH of from about 2 to about 6, and a cross-linked resin binder which comprises the reaction product of a compound having as its sole reacting groups not less than two active hydrogen groups as determined by the Zerewitinoff method and a compound having as its sole reacting groups not less than two groups capable of undergoing a urethane-type reaction with active hydrogen groups.

15. A solid propellant composition which comprises a cured intimate mixture of an oxidizer comprising spherical hydrazine perchlorate having a diameter of from about 10 microns to about 500 microns, containing less than about 0.1 percent by weight of water, said spheres when dissolved in water in an amount from about 20% to about 80% by weight of the total solution, having a pH of from about 2 to about 6, and a cross-linked resin binder which comprises the reaction product of a polyalkylene ether glycol having a molecular weight of from about 400 to about 10,000, and an aromatic diisocyanate.

16. A solid propellant composition which comprises a cured intimate mixture of an oxidizer comprising spherical hydrazine perchlorate having a diameter from about 10 microns to about 500 microns, containing less than about 0.1 percent by weight of water, said spheres when dissolved in water in an amount from about 20% to about 80% by weight of the total solution, having a pH of from about 2 to about 6, and a cross-linked resin binder which comprises the reaction product of polypropylene ether glycol, a tolylene diisocyanate, and glycerol monoricinoleate.

17. A solid propellant composition which comprises a cured intimate mixture of an oxidizer comprising spherical hydrazine perchlorate having a diameter from about 10 microns to about 500 microns, containing less than about 0.1 percent by weight of water, said spheres when dissolved in water in an amount of from about 20% to about 80% by weight of the total solution having a pH of from about 2 to about 6, and a cross-linked resin binder which comprises the reaction product of a hydroxy-terminated polyester, having a molecular weight from about 1,000 to about 2,500, and an aromatic diisocyanate.

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