

[54] **SOLID POROUS, COATED OXIDIZER,
METHOD OF PREPARATION AND NOVEL
PROPELLANT COMPOSITIONS**

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Jacobs

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149/19.91, 149/19.93

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149/19

[57] **ABSTRACT**

A rocket propellant composition having an exception-
ally high burning rate may be prepared by incorporat-
ing therein an oxidizing salt which comprises at least
in part an ammonium salt characterized by a porous
structure.

[56] **References Cited**

UNITED STATES PATENTS

2,969,638 1/1961 Sammons..... 60/219

39 Claims, No Drawings

SOLID POROUS, COATED OXIDIZER, METHOD OF PREPARATION AND NOVEL PROPELLANT COMPOSITIONS

This invention relates to an improved solid oxidizer and to a method for its preparation and to a novel, rapid burning solid projectile or propellant composition.

Solid propellant rocket motors in their early development were primarily employed in tactical, intermediate range and intercontinental ballistic missiles. For these applications the propellant characteristically possessed a moderate burning rate which is adequate for the production of the necessary thrust. Later, it became necessary to provide a solid propellant rocket motor for use in the interception of incoming ballistic missiles. To be successful for the latter application, an antimissile missile must be capable of rising very rapidly from the ground upon receiving directions from a computer and proceeding to a point of interception, sufficiently distant from the ground so that the incoming war heads may be destroyed without endangering the underlying land mass. In order that this may be accomplished, the solid propellant employed in the anti-missile missile must be capable of rapidly producing a large thrust. To achieve the required high acceleration, the propellant must possess a high burning rate.

It has been proposed heretofore to incorporate elongated metal conductors or staples in the propellant composition to obtain high burning rates. The use of metal staples accelerates the burning rate of the propellant composition to a considerable degree; however, the increase in burning rate which may be obtained is less than is sometimes desired and in addition the use of the longitudinal or other irregular shaped metal conductors results in troublesome propellant compounding problems. Solid propellant compositions incorporating metal conductors frequently evidence an anisotropy of the burning rate.

It is a principle object of this invention to provide a solid propellant composition which possesses a sufficiently high burning rate to be suitable for use in an anti-missile missile.

It is a further object of this invention to provide an improved solid oxidizer and a method for its production.

It is another object of this invention to provide a solid propellant composition characterized by a uniform burning rate in all directions throughout the propellant.

These and other objects of the invention will be apparent from the detailed description which follows.

It has now been found that a solid propellant composition of a high and uniform burning rate may be prepared by incorporating therein an oxidizing salt which comprises at least in part a particulate ammonium inorganic salt characterized by a porous structure. The porous ammonium salt is present in an amount effective to significantly increase the burning rate of the propellant composition and while it may totally displace the non-porous salt in some applications, it is usually provided as a minor portion of the oxidizing salt, typically being present in an amount in excess of 1 percent and less than 50 percent, preferably from about 7 to about 28 percent by weight of the total oxidizing salt.

The porous ammonium inorganic salt particles are generally spherical and usually have an average particle

diameter within the range of 5 to 4000 microns. Characteristically the average particle diameter for ammonium salt crystals to be used in a propellant composition will be within the more narrow range of 5 to 250 microns.

The particulate porous ammonium inorganic salt is characterized by voids throughout and has generally a cubicle crystal structure. In a preferred embodiment, the porous salt is provided with a coating over the exterior surface thereof. The coating serves to substantially block the exteriorly-opening pores and may be formed of various materials capable of serving in this role. Typically, the coating will be formed of an organic polymeric material, the preferred coating composition being an alkylene imine adduct of divinyl benzene.

The preferred ammonium salt for use in the invention is ammonium perchlorate, although other ammonium oxidizing salts such as ammonium chromate, ammonium permanganate, ammonium nitrate, ammonium chlorate and the like may be employed.

The effectiveness of the porous ammonium salt in increasing propellant burning rate is believed to be due to its grossly different physical structure from the normal ammonium oxidizing salts rather than to changes in chemical nature. The particulate porous ammonium salt within the propellant composition provide areas where the burning rate is obviously considerably faster than in the propellant matrix and it is thought that the voids within the porous ammonium salt particles play an important role. Characteristically, the porous ammonium perchlorate of the invention or other porous ammonium salt has an individual particle density within the range of about 1.2 to 1.75 grams per cubic centimeter, and preferably about 1.35 to about 1.65 grams per cubic centimeter. The porous salt possess a bulk or packing density generally within the range of about 0.6 to 1.0 grams per cubic centimeter, and preferably about 0.75 to about 0.9 grams per cubic centimeter. In the latter density determination, the porous ammonium salt particles are poured into a cylinder and the cylinder vibrated until the composition acquires a constant bulk density.

The porous ammonium oxidizing salt of the invention is prepared by heating the ammonium perchlorate or other ammonium salt to effect a partial decomposition and a change from an orthorhombic crystal structure to a cubicle structure. While the heating may be conducted at various different temperatures, for example, in the range of about 180°C to about 400°C. Typically in the instance of ammonium perchlorate the salt is exposed to a temperature in the range of 180° to 350°C, preferably within the range of 240° to 280°C for a period of time to achieve a weight loss within the range of about 20 to about 35 percent. Heating results in an evolution of gas, leaving a residue which is entirely ammonium perchlorate and crystals which have become porous. The curve of percent weight loss versus time consists of an induction period during which no significant weight loss occurs, followed by an acceleratory period during which the weight loss increases, and a deceleratory period during which the weight rate decreases. When employing a temperature in the range of about 200° to 280°C, the decomposition of the ammonium perchlorate levels off after approximately 30 percent decomposition. It has been found that changes in particle size of the ammonium perchlorate do not appreciably effect the induction or acceleration periods

but affect the deceleratory period with smaller particles decomposing faster than large particles. It has been demonstrated that decomposition may be achieved either in air at atmospheric pressure or in a partial vacuum or in an inert atmosphere. In the instance of decomposition in air at atmospheric pressure the weight loss levels off at approximately 32 percent.

A particularly important characteristic of partially decomposed particulate ammonium salt, as it relates to its use as a component in fast-burning propellants, is the porosity of the crystals. Photomicrographs of heated ammonium perchlorate clearly reveal the porosity. An individual particle or crystal decomposes initially only at the surface but eventually throughout the crystal, apparently along intermosaic boundaries. Microscopic studies show that two types of pores are obtained, one type of pore being sealed inside the crystal and the other type connected with the surface by "tunnels".

In a preferred manner of preparing the porous ammonium salt, the decomposition is achieved by heating, for example, thin layers of about 0.3 inch thick of the ammonium salt at 260°C (in the instance of ammonium perchlorate) for about 30 minutes in a vented oven. The porous product is then cooled to ambient temperature and degassed in a vacuum for a period of time, typically for 24 hours, adequate to remove residual decomposition products. It will be appreciated that the thickness of the salt layer may vary but will generally be less than one inch and preferably less than one-half inch. The porous product is then stored under dry nitrogen or other suitable dry conditions, prior to use, to prevent recrystallization and healing of the pores which would occur if the porous product were stored under moist conditions.

The porous ammonium perchlorate or other ammonium salt from the heating operation may be incorporated without further processing into the high burning rate propellant composition; including other applications, such as explosives, ammunition, and stop-start propellant motors. However, in the preferred embodiment the porous salt is coated to accomplish a substantially complete closing of the exteriorly-opening pores. The uncoated porous ammonium salt may be satisfactorily incorporated in the propellant composition providing mixing is accomplished at atmospheric pressure. A composition mixed at atmospheric pressure will have a high burning rate; however, where the mixing is accomplished under vacuum with the uncoated ammonium perchlorate, the mix will generally go "dry." The dry condition under subsequent microscopic examination has been shown to be due to an absorption of liquid ingredients into the tunnel pores of the porous structure. The absorption occurring under a vacuum mixing may be avoided by first coating the porous ammonium salt with a compatible material. The coating which is generally an organic polymer will comprise typically from about 3 to about 8 percent, generally less than 5 percent of the weight of the ammonium salt.

The improvement in propellant burning rate is believed to be attributable to a void mechanism. The voids or pores created in the ammonium crystals contain gasses generally at or near atmospheric pressure. During burning of the propellant, the high pressure of the advancing flame front reaches the porous ammonium salt and hot combustion gasses press into the interior of the porous salt crystal, accomplishing an igni-

tion of the whole volume of the crystal and thereby bringing about almost instantaneous combustion of the ammonium salts.

While the uncoated porous ammonium salt provides a significant increase of propellant burning rate its results are less certain and additionally the propellant mixing process is more difficult. In one controlled test, a porous ammonium perchlorate containing propellant composition evidenced a burning rate of 3.4 inches per second, at 2,000 psi in contrast to a burning rate of 6.0 inches per second for a coated ammonium perchlorate propellant composition while a propellant composition containing no porous ammonium perchlorate but a like quantity of normal ammonium perchlorate exhibited a burning rate of 1.7 inches per second. The porous ammonium perchlorate incorporated in the coated and uncoated examples comprised approximately 28 percent of the total weight of the ammonium perchlorate oxidizing salt. It has been noted that porous ammonium perchlorate prepared from larger crystal sizes of particulate ammonium perchlorate produces a stronger effect than that prepared from smaller sized particles of the oxidizers. For example, porous ammonium perchlorate obtained from a particularly large particle size ammonium perchlorate (approximately 2,500 microns) gave burning rates of 8.2 inches per second at 2,000 psi.

Various procedures and compositions may be employed to coat the porous ammonium salt. A preferred procedure involves the use of a solution of ethylene imine adduct of divinyl benzene in hexane or other hydrocarbon or chlorinated hydrocarbons. The ethylene imine adduct is extracted from solution onto the surface of the porous ammonium salt and there homopolymerizes to form a coating over the salt crystal. The ammonium perchlorate or other ammonium salt catalyzes the homopolymerization of the alkylene imine adducts of divinyl benzene. The coating seals the outer pores of the porous ammonium salt crystal and prevents the latter pores from filling up with binder material during the mixing of the propellant composition. The coating also improves the physical properties and castability of the propellant. Other lower alkylene imine adducts of divinyl benzene including propylene imine, butylene imine have been investigated and found to be suitable. Various hydrocarbon solvents may be used in the place of hexane or along with the hexane including an hydroxy-terminated polybutadiene.

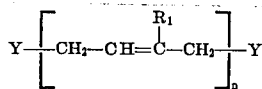
Hydroxy-terminated polybutadiene and other functional-terminated polybutadienes in the presence of a suitable catalyst such as normal butyl ferrocene may be used for forming a coating for the porous ammonium salt crystals. However, the polybutadiene materials are highly viscous and difficult for this reason to use. It has been found possible to modify the imine adduct polymer by incorporating a small amount of hydroxy-polybutadiene in the hydrocarbon solution. In one coating procedure, an excess of a 10 percent solution of the alkylene imine adduct of divinyl benzene in hexane is permitted to stand with the porous ammonium salt at room temperature for approximately 12 hours with an occasional agitation. The hexane is then decanted and the coated porous ammonium salt washed with additional fresh hexane. Thereafter, the washed material is dried in a thin layer at a moderately elevated temperature, for example, 50°C - 72°C. In the second

procedure, a 5 percent solution of the alkylene imine adduct of divinyl benzene in hexane is added to the ammonium salt and the mixture tumbled in a rotary dryer at a moderately elevated temperature, for example 57° - 60° for 24 hours or thereabout. The hexane is then removed under vacuum.

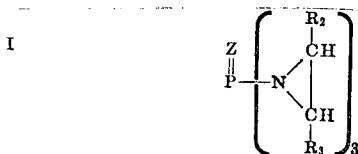
In a presently preferred method of coating the porous ammonium perchlorate, an alkylene imine adduct of divinyl benzene, preferably the ethylene imine adduct, is placed in a one to one solution of hexane or heptane. 400 grams of porous ammonium perchlorate or other ammonium salt is placed in a slurry of 288 grams of hexane or heptane. The hexane solution of the alkylene imine adduct is added slowly with stirring to the ammonium perchlorate slurry. Mixing is continued for at least 2 hours with the temperature being maintained at 60°C. The excess liquid is decanted and the coated porous ammonium perchlorate is dried at a temperature in the range of 60° - 70°C for about 16 to 24 hours. In still another approach 20 grams of the ethylene imine adduct or other alkylene adduct of divinyl benzene is added to approximately 288 grams of hexane and thoroughly mixed. 400 grams of porous ammonium perchlorate or other porous salt is slowly added to the solution with constant stirring. Mixing continues for 20 hours at a temperature of approximately 20°C. The excess liquid is decanted and the coated particles dried in an oven at 70°C for 16 to 24 hours.

It is contemplated that the porous ammonium salt of the invention in either its coated or uncoated form may be incorporated in various propellant compositions. In some instances it may be desirable to use the porous salt along with metal staples to obtain further increase in burning rate. Additionally, it is contemplated that various conventional burning rate catalysts such as copper chromite or normal butyl ferrocene may be used in varying amounts, for example, from about 0.01 to 6 percent by weight of the total propellant in conjunction with the porous ammonium salt. The propellants may also contain from about 1 to about 20 percent by weight of powdered metals such as aluminum. Various known binders or fuels may be employed in combination with the porous ammonium salt oxidizing agent. Propellants of this invention can be conveniently ignited by a conventional igniter, for example, the igniter disclosed in Assignee's U.S. Pat. No. 3,000,312, issued Sept. 19, 1961.

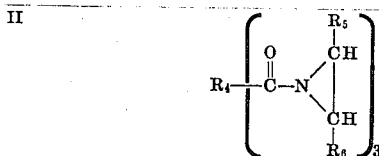
A preferred class of binders for use in the rapid burning propellants of the present invention are the reaction products of a functional-terminated polydiolefin of the formula:



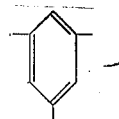
wherein R₁ is hydrogen or methyl, Y is a functional terminal group selected from the class consisting of carboxy, hydroxy, amine and mercapto; and n is an integer of from 8 to about 50; and an aziridinyI curing agent of one of the following types:



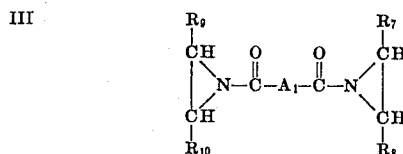
wherein Z is oxygen or sulfur; and R₂ and R₃ are hydrogen or lower alkyl such as methyl, ethyl and pentyl;



wherein R₄ is a trivalent organic radical of the formula:



and R₅ and R₆ is hydrogen or lower alkyl of from 1 to about 4 carbons; and



wherein A₁ is alkylene, preferably lower alkylene of from 1 to about 12 carbons, and R₇, R₈, R₉ and R₁₀ are hydrogen or lower alkyl of from 1 to about 4 carbons. Normally, the aziridinyI curing agent is employed in an amount from 1 to about 40 parts per 100 parts of the functionally-terminated polydiolefin. The preferred polydiolefin of the above formula is polybutadiene or polyisoprene having a molecular weight of from about 400 to about 5,000, a viscosity at 77°F of from about 5 to about 500 poise, and is carboxy-terminated (Y = COOH).

Typical aziridinyI curing agents within the scope of the foregoing formula include:

tris(N-1', 2'-butylene)trimesamide,
tri(2-methyl-3-n-butyl-1-aziridinyI)phosphine oxide,
tri(2-ethyl-3-octadecyl-1-aziridinyI)phosphine oxide,
tri(2-methyl-3-cyclopentyl-1-aziridinyI)phosphine oxide,
tri(2-methyl-3-benzyl-1-aziridinyI)phosphine oxide,
tri(1-aziridinyI)phosphine sulfide,
tri(2-methyl-1-aziridinyI)phosphine sulfide,
tri(2-eicosyl-1-aziridinyI)phosphine sulfide, and
tri(2-methyl-3-cyclohexyl-1-aziridinyI)phosphine sulfide.

The polyurethane binders which can be used in my propellants are prepared by reacting a compound having two or more active hydrogen containing groups capable of polymerizing with an isocyanate as determined by the Zerewitinoff method, with an organic compound having as the sole reacting groups, two or more isocyanate or isothiocyanate groups. The active hydrogen containing groups are preferably hydroxyl or thiol.

It will be apparent that, where more than two active hydrogen, isocyanate, or isothiocyanate groups are present in any of the polyurethane reactants, the structure of the polyurethane binder will contain at least some cross-linking. Where bifunctional reactants, such as dihydroxy compounds and diisocyanates are employed to produce the polyurethane binders for our novel propellants, it is necessary to also employ a "cross-linking" agent to provide a product having a

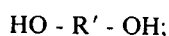
cross-linked structure. Compounds suitable as cross-linking agents for the polyurethane binders are those compounds having as the sole reacting groups at least three groups polymerizable with active hydrogen or isocyanate groups.

Examples of compounds which we have found to be particularly suitable as cross-linking agents are 1,2,6hexanetriol; methylene *bis*-(*ortho*chloroaniline); monohydroxyethyl trihydroxypropyl ethylenediamine; N,N,N', N-tetrakis (2-hydroxypropyl) ethylenediamine; triethanolamine; and trimethylolpropane.

A wide variety of polyurethane binders for the propellants of this invention can be prepared by varying the starting materials. These polyurethane binders are disclosed in greater details in Assignee's co-pending applications Ser. No. 829,180 and Ser. No. 829,182, both filed July 23, 1959.

The preferred diisocyanate compounds are saturated or unsaturated; aliphatic or aromatic; open or closed chain; and substituted or not be groups substantially unreactive with isocyanate or hydroxyl groups such as ketone or ether groups. Diisocyanate compounds such as tetramethylene diisocyanate, decamethylene diisocyanate; *m*-phenylene diisocyanate; diphenylene-4,4-diisocyanate; 2,4-tolylene diisocyanate; 3-nitro-1,3-pentane diisocyanate; duren diisocyanate; and 2,6-tolylene diisocyanate are particularly suitable as reactants for the preparation of polyurethane binders.

The preferred hydroxy starting materials for the polyurethane binders are dihydroxy compounds having the general formula:



where R' is a divalent organic radical, such as alkylene or arylene. 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.

Other dihydroxy compounds suitable for the polyurethane reaction of this invention are 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 purposes of this invention are those having a molecular weight from about 1000 to about 2,500.

In addition to the polyesters, polyethers such as polyethylene ether glycols, polypropylene ether glycols, other polyalkylene ether glycols, and mixtures or copolymers thereof having molecular weights of from about 200 to about 10,000 can be utilized as dihydroxy reactants of the polyurethane reaction of this invention.

Other binders which may be employed in my novel propellants include resinous binders such as rubbers, polysulfides, and rubber-polysulfide mixtures.

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 polychloroprene. 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.

Still other examples of polymeric organic material suitable as binders are phenol-aldehyde resins, polyester resins, acrylate resins and polyalkylene resins.

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

Saturated polycarboxylic acids useful in compounding the polyester resins are, for example, the aliphatic dibasic acids, including oxalic, malonic, succinic, glutaric, adipic, pimelic, sebacic and azelic. The unsaturated acids useful as the acidic components in forming polyester resins are maleic acid, fumaric acid, citraconic acid and mesaconic acid, itaconic acid. The anhydrides such as itaconic anhydrides and phthalic anhydride may also be used to supply the desired unsaturation.

Regardless of which of the saturated acids are used, the degree of unsaturation necessary to provide cross-linking with the ethylenically unsaturated components may be obtained by the addition of any of the above-named unsaturated acids or their anhydrides.

The alcohols that can be used are not limited to the dihydric alcohols as other polyhydric alcohols such as the trihydric and higher polyhydric alcohols may be used. For the polyhydric alcohol component any of the following alcohols may be used: dihydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol and propylene glycol; a trihydric alcohol such as glycerol; tetrahydric alcohols such as the erythritols and pentaerythritols; pentitols which include arabitol, adonitol and xylitol; hexatols including mannitol, sorbitol and dulcitol; heptitols such as persitol and volamitol; or mixtures of any of the above alcohols may be also employed if desired.

The ethylenically unsaturated component of the polyester resin binders may be styrene, vinyl acetate, methyl methacrylate, allyldiglycol carbonate, diallyl maleate, diallyl glycolate, propylene, butadiene, etc.; as well as derivatives of any of the above substances which are capable of polymerization with the polyester resin.

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.

Acrylate resin binders within the scope of this invention comprise copolymers of any two or more reduced oxygen-containing polymerizable monomers such as alkenoic acids, alkenoic acid esters, dialkenyl diglycolates, dialkylene diglycol *bis*-(alkenyl carbonate), alkenyl phthalates, etc. Examples of reduced oxygen-containing polymerizable monomers suitable for acrylate propellant binder formation are the acrylates and methacrylates such as methyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, butyl methacrylate, propyl methacrylate, diethyleneglycol *bis*-(allyl carbonate), diallyl phthalate, diallyl diglycolate, diallyl maleate and diallyl fumarate.

Other acrylate binders suitable for use in my invention are prepared by copolymerizing polymerizable substances containing reduced oxygen in the molecule, such as the nitro and nitroether-substituted alkenoic acids and esters. Specific examples of nitro-containing monomers which copolymerize to form acrylate propellant binders are 2-nitroethyl acrylate; the nitrobutyl acrylates; 2,2-dinitropropyl acrylate; 2,2,3,3-tetranitrobutyl acrylate; and 2,2,3,3-tetranitrobutyl methacrylate.

Still other acrylate binders comprise copolymers of any one or more of the above-mentioned reduced oxygen-containing monomers and any one of more of the above-mentioned monomers containing unreduced oxygen in the molecule. These binders, as well as those acrylate binders referred to above, and their methods of preparation are more fully described in Assignee's copending U.S. application Ser. No. 321,941, filed Nov. 21, 1952, and now abandoned.

Polyurethane resins containing unreduced oxygen are suitable binders for the propellants of my 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. application, Ser. No. 728,491, filed Apr. 14, 1958.

Illustrative of other solid propellant binders suitable for use in the novel propellants of this invention are those disclosed in U.S. Pat. 2,479,828 and British Pat. No. 579,057.

Another class of binder materials useful in the preparation of the propellants of this invention are the low molecular weight isoolefin-polyolefin copolymers of the type disclosed in Assignee's copending U.S. application Serial No. 202,351, filed June 8, 1962.

Still other types of binders suitable for use in my novel solid propellant composition are nitrocellulose-plasticizer binders of the type prepared by curing mixtures of finely divided nitrocellulose and suitable plasticizers such as pentaerythritol trinitrate. Binders of this type and their methods of preparation are well-known to those skilled in the propellant art.

A finely divided nitrocellulose suitable for use in the preparation of the subject binders is obtained by first dissolving nitrocellulose, preferably prepared from cotton linters, in a solvent such as an ethyl acetate-acetone mixture, an ethyl acetate-ethanol mixture, or nitromethane to form a lacquer. The lacquer is slurried in an aqueous medium containing a suspending agent such as methyl cellulose in combination with an emulsifier such as turkey red oil and an agent to prevent agglomeration such as, for example, sodium chloride as a result of which the nitrocellulose precipitates from the solvent and is recovered as a particulate material having an average particle size of 10 to 12 microns and an overall particle size range of from about 1 to about 35 microns. Finely divided nitrocellulose prepared by the above-described method is known to those skilled in the art as plastisol grade nitrocellulose and will be hereinafter referred to as such. Plastisol grade nitrocellulose is readily available on the open market.

Various additives may be employed in preparing the binders of this invention. For example, plasticizers, such as, isodecyl pelargonate, polybutene, dioctyl azelate, *bis*-(2,2-dinitropropyl) formal and *bis*-(2,2-dinitropropyl) acetal may be utilized. Also catalysts such as ferric acetylacetonate and boron trifluoride can be employed if desired. The catalysts can be employed

in quantities within the range from mere traces up to amounts equivalent to about one percent by weight of the total propellant composition. Normally amounts of from about 0.02 to about 0.10 percent by weight are employed. Other additives such as antioxidants, wetting agents, anti-foaming agents, etc., can be employed, if desired, in the formulation of the novel propellants.

Because higher temperatures tend to produce shrinkage and internal strains, it is preferable to carry out the cure at temperatures in the range of from about 70° to about 180°F. Within this range the reaction rate is sufficiently rapid for economical production. Yet the temperature is not so high as to produce shrinkage and internal stresses which must be avoided at all costs - especially in the case of large solid propellant motors.

Those skilled in the art will appreciate the fact that heating and cooling steps can be incorporated into the propellant processing procedure to attain optimum operating conditions for producing a given specific propellant. Likewise, various techniques which may serve to optimize the processing procedure or improve the quality of the product, e.g. vacuumizing the mixture during certain phases of the operation, can be employed if desired. The various processing steps can be carried out with standard equipment well-known to those skilled in the art. The mixer can be equipped with facilities for heating, cooling, and vacuumizing propellant batches during mixing.

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, oxidizer, plasticizer, etc., selected and size of the batch to be prepared.

The propellant binder will be employed in amounts generally characteristic of the art and preferably is used in a proportion within the range from about 5 to about 55 percent by weight of the total propellant composition with the inorganic oxidizing salt, including the porous ammonium salt, being present in an amount within the range from about 95 to about 45 percent by weight. The burning rate of the propellant composition may be widely varied by adjusting the ratio of the porous ammonium salt to the non-porous oxidizing salt but typically the porous ammonium salt will be present in a minor portion and generally in the amount from about 7 to 28 percent by weight of the total oxidizing salt.

The following examples are included for purposes of illustrating the novel oxidizer salt, its process of manufacture and the propellant composition of the invention. These examples are intended for illustrative purposes only and should not be construed as limitations of the scope of the invention to the particular conditions and embodiments set forth herein.

Example I

Particulate ammonium perchlorate having an average particle diameter of 125 microns is placed in a layer of approximately 0.3 inches thick and exposed to a temperature of 265°C for 30 minutes in a vented oven. At the end of the heating period, the crystals are decomposed to an extent of about 23 percent by weight. The crystals are then degassed in a partial vacuum for about 24 hours to remove residual acidic decomposition products. The resulting porous ammonium perchlorate crystals have a typical individual par-

ticle density of about 1.5 grams per cubic centimeter and a bulk density of 0.8 grams per cubic centimeter.

The porous ammonium perchlorate product is coated with methylaziridinyl adduct of divinyl benzene. A 5% solution of the methylaziridinyl adduct of divinyl benzene in heptane is prepared. The porous ammonium perchlorate is dispersed in a heptane carrier there being 500 grams of the oxidizer salt per one liter of the heptane. The heptane solution of the adduct is added slowly with vigorous stirring to the oxidizer heptane slurry at 60°C. The adduct heptane solution is added to the oxidizer slurry in the amount of approximately 40 milliliters per one liter of the oxidizer heptane slurry. Slow stirring is continued for approximately four hours and then the porous ammonium perchlorate is filtered and dried at approximately 60°C.

Example II

Particulate ammonium perchlorate having an average diameter of 200 microns was heated in a layer of about 0.4 inches thick at 265°C in a vented oven for approximately 30 minutes. The crystals were then degassed in a vacuum for 24 hours. The heating brought about a weight loss of approximately 22 percent, giving a porous ammonium perchlorate having an individual particle density of approximately 1.5 grams per centimeter and a bulk density of .8 grams per centimeter. The porous ammonium perchlorate crystals were coated using the general process of Example I, employing as the coating material (methylaziridinyl adduct of divinyl sulfone) for a portion of the porous product with the balance being coated with methylaziridinyl adduct of divinyl benzene.

Example III

Particulate ammonium perchlorate having an average particle diameter of 500 microns was heated at a temperature of 200°C for 16 hours to effect a weight loss of approximately 30 percent. Thereafter, the decomposed ammonium perchlorate was held in a partial vacuum for approximately 24 hours to remove residual decomposition products. The resulting porous ammonium perchlorate crystals evidenced an individual particle density of 1.6 grams per cubic centimeter and a bulk density of 0.85 grams per cubic centimeter. The porous ammonium perchlorate product is coated by introducing the particulate material to a bath of hydroxy-terminated polybutadiene which contains, as a catalyst approximately 1 percent normal butyl ferrocene. The polybutadiene is rather cumbersome to use because of its high viscosity. Excess polybutadiene is washed from the coated crystals by employing heptane and dried at 60°C.

Example IV

Porous ammonium perchlorate is prepared as in Example III and coated in a bath of carboxy-terminated polybutadiene containing 1 percent normal butyl ferrocene. Polybutadiene is then decanted and the coated porous ammonium salt washed with hexane. Thereafter the washed material is dried at approximately 50°C.

Example V

Porous ammonium perchlorate is prepared as in Example I and permitted to stand for fourteen hours in a 10 percent solution of ethylene imine adduct of divinyl benzene in hexane. The hexane is then decanted and

the coated porous ammonium salt washed with additional fresh hexane. The washed coated salt crystals are then dried at approximately 60°C.

Example VI

Particulate ammonium perchlorate is prepared and coated in accordance with the process of Example V with the difference being that the alkylene imine adduct hexane solution contain a small amount of hydroxy-terminated polybutadiene, the polybutadiene being present in approximately 90 percent of the weight of the imine adduct.

Example VII

Porous ammonium nitrate salt having an average diameter of 100 microns is prepared in accordance with the heating process of Example I and coated with propylene imine adduct of divinyl benzene. A 5 percent solution of the propylene imine adduct in hexane is added to the porous ammonium salt and the mixture tumbled in a rotary dryer at a temperature of approximately 60°C for 18 hours. The hexane is then removed under vacuum to leave a dry coated porous product.

Example VIII

The coated porous ammonium chlorate product of the instant example is prepared in accordance with Example VII with the difference being that the coating is formed of the butylene imine adduct of divinyl benzene.

Example IX

A particulate porous ammonium perchlorate salt is prepared by the heating process of Example I and one portion coated with ethylene imine adduct of divinyl benzene is prepared in accordance with the general procedure of Example I. Three propellants, all of equal solids content are prepared. In propellant A the ammonium perchlorate salt is of the conventional type and present in an amount of 72 percent by weight of the total propellant composition. Propellant B contains 52 percent by weight of the normal ammonium perchlorate salt and 20 percent by weight of the porous ammonium perchlorate (uncoated). Propellant C contains 52 percent by weight of normal ammonium perchlorate and 20 percent by weight of coated porous ammonium perchlorate. The ammonium perchlorate has an average particle diameter of 600 microns. Each of the three propellant compositions contains in addition 12 percent aluminum powder, 5 percent normal butyl ferrocene, and 11 percent of aziridine-cured polybutadiene polymer. The propellant compositions are prepared in accordance with standard mixing practice with, as indicated, in the instance of propellants B and C, a portion of the normal ammonium perchlorate having substituted therefore the porous product. The three propellants were tested using a three-inch Crawford bond strand burning test at 2,000 psi with the following results:

Table I

Propellant A	1.7 inch/per second
Propellant B, uncoated	3.4 inch/per second
Propellant C, coated	6.1 inch/per second

As can be seen from the foregoing data, the incorporation of the porous ammonium perchlorate, either

coated or uncoated, substantially increases the burning rate of the propellant.

Example X

In the instant example three different particle sizes of porous ammonium perchlorate coated with ethylene imine adduct of divinyl benzene are used to demonstrate the effect on burning rate and pressure exponent. The porous ammonium perchlorate is prepared in accordance with the process of Example I. The three average particle sizes as 600 microns, 400 microns, and 180 microns. The porous ammonium perchlorate is incorporated in the formulation of the preceding example in an amount of 15 percent by weight of the total propellant composition with the balance of the oxidizing salt being normal ammonium perchlorate. The 180 micron porous ammonium perchlorate at the 15 percent level, produces a burning rate of 3.5 inch/per second at 2,000 psi and a pressure exponent of 0.6. The 400 micron average particle size porous ammonium perchlorate produces a burning rate of 4.1 feet/per second at 2000 psig and a pressure exponent of approximately 0.97. The 600 micron porous ammonium perchlorate, at the 15 percent level produces a burning rate of 5.0 inches/per second at 2,000 psig and a pressure exponent of approximately 1.4. It will be seen that in the instant example, the 180 micron size porous ammonium perchlorate with the lower pressure exponent is more desirable for ballistic application.

Example XI

In the instant example, the porous ammonium perchlorate having an average particle diameter of 180 microns is coated with 3 percent by weight of ethylene imine adduct of divinyl benzene. The porous product is prepared in accordance with Example II. The porous ammonium perchlorate is incorporated in the propellant formulation set forth below in an amount of 15 percent by weight of the total composition. The balance of the ammonium perchlorate solution is normal ammonium perchlorate and is provided in two different particle sizes as indicated.

Ingredient	Composition, %
Ammonium perchlorate 7-9 microns	39.0
Ammonium perchlorate 125 microns	17.0
Porous ammonium perchlorate 180 microns	15.0
Aluminum powder (H-60)	14.0
n-butylferrocene	5.0
Carboxy-terminated polybutadiene (100 eq.)	
Butylene imine adduct of sebacic acid (95 eq.)	
tris 1-(2-methyl) aziridinyl phosphene oxide (90 eq.)	10.0
	100.0

The propellant composition is mixed and cast by standard procedures the propellant has good flow characteristics and exhibits the properties set forth in Table II.

Table II

Burning rate	
Crawford bomb solid strands, inch/sec at 2000 psia	3.5
3KS-500 motors, extraplated	3.4
Pressure exponent	
Crawford bomb	0.60
3KS-500 motors	0.47

The instant invention contemplates the use of various available binders, plasticizers, catalysts, and other additives in combination with the improved porous oxidizer. Known propellant mixing techniques may be employed for the manufacture of the improved propellants with the porous salt oxidizer being incorporated into the mixture along with the normal oxidizing salt. Typical mixing procedures for the manufacture of metal staple containing propellants are set forth in co-pending Assignee's U.S. Ser. No. 338,527, filed Jan. 16, 1964. The following compositions are contemplated as being generally representative of the wide variety of formulations that may advantageously incorporate the porous ammonium salt.

Example XII

Ingredient	Weight Percent
Ammonium perchlorate, normal	66.50
Porous ammonium perchlorate	15.00
Powdered aluminum	1.00
Isodecyl pelargonate	3.50
Lecithin	0.24
Aluminum staple (0.5 × 4.0 × 62 mil)	4.00
Copper chromite	1.50
Carboxy-terminated polybutadiene	7.40
Tris-(2-methyl aziridinyl) phosphine oxide	0.86
	100.00

Example XIII

Ingredient	Weight Percent
NH ₄ NO ₃ , normal	65.50
NH ₄ NO ₃ , porous	10.00
(NH ₄) ₂ Cr ₂ O ₇	1.80
Polyester from 7 moles of adipic acid, 3 moles of maleic anhydride and 11 moles of diethylene glycol	8.80
Styrene	2.22
Methyl acrylate	11.00
Lecithin	0.03
Methyl ethyl ketone peroxide	0.45
t-Butyl catechol	0.20
	100.00

Example XIV

Ingredient	Weight Percent
Ammonium perchlorate, normal	61.50
Ammonium perchlorate, porous	20.00
Aluminum staple (0.5 × 4.0 × 62 mil)	2.00
Polypropylene glycol	9.63
Glycerol monoricinoleate	1.18
Dioctyl azelate	3.62
Ferric acetylacetonate	0.04
Phenyl betanaphthylamine	0.20
Lecithin	0.21
Tolyene diisocyanate	1.62
	100.00

Example XV

Ingredient	Weight Percent
Ammonium perchlorate, normal	67.00
Porous ammonium perchlorate	18.00
Lecithin	0.20
Phenyl betanaphthylamine	0.20
Polytetramethylene ether glycol	8.95
Glycerol monoricinoleate	1.10
Diocetyl azelate	3.00
Ferric acetylacetonate	0.04
Tolylene diisocyanate	1.51
	100.00

Example XVI

Ingredient	Weight Percent
Ammonium Perchlorate, normal	66.50
Ammonium Perchlorate, porous	19.00
Powdered Aluminum	1.00
Copper Chromite	1.50
Isodecyl Pelargonate	3.50
Lecithin	0.20
Carboxy terminated polybutadiene (M.W.-6000)	7.93
Succinic Anhydride-Diethanol Amine Adduct	0.07
Tris N-1',2'-Butylene)Trimesamide	0.20
Tris(1-Aziridinyl)Phosphine Oxide	0.10
	100.00

It will be understood that various modifications may be made in this invention without departing from the spirit thereof or the scope of the appended claims.

I claim

1. An improved solid oxidizer comprising a particulate porous ammonium inorganic salt characterized by voids throughout and a compatible coating over the exterior surface thereof, said coating substantially sealing the exterior openings of the pores of the ammonium salt without filling such pores.

2. An improved solid oxidizer comprising a particulate porous ammonium inorganic salt characterized by an average individual particle density of 1.2 to 1.75 grams per cubic centimeter and a compatible coating over the external surface thereof, said coating substantially sealing the exterior openings of the pores of the ammonium salt without filling such pores.

3. An oxidizer in accordance with claim 2 wherein the ammonium inorganic salt is selected from the group consisting of a chromate, permanganate, nitrate, chlorate, and perchlorate.

4. An oxidizer in accordance with claim 2 wherein the ammonium inorganic salt particles are generally spherical and have an average particle diameter within the range of 5 to 4,000 microns.

5. An oxidizer in accordance with claim 2 wherein the ammonium salt particles are generally spherical and have an average particle diameter within the range of 5 to 250 microns.

6. An oxidizer in accordance with claim 2 wherein the coating is formed of an organic polymeric material.

7. An oxidizer in accordance with claim 6 wherein the oxidizer particles are coated with an alkylene imine adduct of divinyl benzene.

8. An oxidizer in accordance with claim 2 wherein the coating comprises 3 to 8 percent by weight of the ammonium salt.

9. An oxidizer in accordance with claim 2 wherein

the inorganic salt is ammonium perchlorate and the salt has a bulk density of 0.6 to 1.0 grams per cubic centimeter.

10. A process of forming an improved solid oxidizer comprising:

effecting a partial decomposition of a particulate inorganic ammonium salt through heating to achieve a porous structure; and

thereafter coating the porous particulate ammonium salt, said coating being compatible with the ammonium salt and substantially sealing the exterior openings of the pores of the ammonium salt without filling such pores.

11. A process of forming an improved solid oxidizer comprising:

effecting a partial decomposition of a particulate inorganic ammonium salt through heating at a temperature within the range of 200° to 350°C to achieve a porous structure and a weight loss within the range of about 20 to about 35; and

thereafter coating the porous particulate ammonium salts with a compatible organic polymeric material, said coating substantially sealing the exterior openings of the pores of the ammonium salt without filling such pores.

12. A process in accordance with claim 11 wherein the coating is an alkylene imine adduct of divinyl benzene.

13. A process in accordance with claim 12 wherein the alkylene imine adduct is the adduct of ethylene imine and divinyl benzene.

14. A process in accordance with claim 12 wherein the coating is achieved by immersing the porous ammonium salt particles in a hydrocarbon solution of the alkylene imine adduct, whereby the adduct is extracted from the solution onto the porous ammonium salt particles and polymerized on the surface thereof, said ammonium salt serving to catalyze the polymerization reaction.

15. A process in accordance with claim 12 wherein the hydrocarbon solution contains in addition to the alkylene imine adduct a non-volatile, functional-terminated polybutadiene.

16. A process in accordance with claim 11 wherein the ammonium salt is selected from the group consisting of a chromate, permanganate, nitrate, chlorate, and perchlorate.

17. A process in accordance with claim 11 wherein the ammonium salt is ammonium perchlorate.

18. A process in accordance with claim 11 wherein the ammonium salt particles are generally spherical and have an average diameter within the range of about 5 to 800 microns.

19. A process in accordance with claim 11 wherein the porous particulate ammonium salt prior to coating is degassed in a substantial vacuum to remove residual decomposition products.

20. A process in accordance with claim 11 wherein the porous ammonium salt is characterized by an average individual particle density of 1.35 to 1.65 per cubic centimeter.

21. A process in accordance with claim 11 wherein the porous ammonium salt is characterized by a bulk density of 0.75 to 0.9 grams per cubic centimeter.

22. A process in accordance with claim 11 wherein the polymeric coating comprises 3 to 8 percent by

weight of the ammonium salt.

23. A solid propellant composition comprising a cured intimate mixture of a resin binder and an inorganic particulate oxidizer salt, said oxidizer salt comprising at least in part a porous ammonium salt characterized by voids throughout and present in an amount effective to significantly increase the burning rate of the propellant composition.

24. A solid propellant composition in accordance with claim 23 wherein the porous ammonium salt comprises a minor portion of the oxidizer salt.

25. A propellant composition in accordance with claim 23 wherein the porous ammonium salt comprises by weight about 7 to about 28 percent of the total oxidizer salt.

26. A propellant composition in accordance with claim 23 wherein the ammonium salt is selected from the group consisting of chromate, permanganate, nitrate, chlorate, and perchlorate.

27. A propellant composition in accordance with claim 23 wherein the porous ammonium salt used in the compound has a bulk density of 0.75 to 0.9 grams per cubic centimeter.

28. A solid propellant composition which comprises a cured intimate mixture of resin binder and a particulate ammonium inorganic oxidizer salt, said oxidizer salt comprising at least in part a porous ammonium salt characterized by an average individual particle density within the range of 1.35 to 1.65 gams per cubic centimeter, said porous salt being present in an amount effective to significantly increase the burning rate of the propellant composition.

29. A solid propellant composition in accordance with claim 28 wherein the porous ammonium salt comprises a minor portion by weight of the total ammonium salt content.

30. A solid propellant composition in accordance with claim 28 wherein the porous ammonium salt com-

prises from about 7 to about 28 percent by weight of the total ammonium salt content of the propellant composition.

31. A propellant composition in accordance with claim 28 wherein the ammonium inorganic salt is selected from the group consisting of a chromate, permanganate, nitrate, chlorate, and perchlorate.

32. A solid propellant composition in accordance with claim 28 wherein the porous ammonium salt has a coating over the surface thereof.

33. A solid propellant composition in accordance with claim 32 wherein the coating on the porous ammonium salt is an organic polymeric material.

34. A solid propellant composition in accordance with claim 33 wherein the polymeric coating is an alkylene imine adduct of divinyl benzene.

35. A solid propellant composition in accordance with claim 28 wherein the resin binder is the reaction product of a functional-terminated polydiolefin and an imine curing agent.

36. A solid propellant composition comprising an inorganic particulate oxidizer salt, said oxidizer salt comprising at least in part a porous ammonium inorganic salt characterized by a cubicle crystal structure and a reducing agent comprising a resin binder for reaction with said oxidizer salt.

37. A solid propellant composition in accordance with claim 36 wherein the porous ammonium inorganic salt has an average individual particle density within the range of 1.2 to 1.75 grams per cubic centimeter.

38. A solid propellant composition in accordance with claim 36 wherein the ammonium inorganic salt is ammonium perchlorate.

39. A solid propellant composition in accordance with claim 36 wherein the porous ammonium salt has a compatible polymeric coating over the surface thereof.

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