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TREATED AMMONIUM NITRATE

Hans H. Ender, Buffalo, N.Y., assignor to Union Carbide Corporation, a corporation of New York
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This invention relates to treated ammonium nitrate and, more particularly, to organosiloxane-coated ammonium nitrate.

Solid propellant compositions containing ammonium nitrate as an oxidizing agent and a solid organic polymer as a fuel have been employed heretofore to supply thrust for rocket engines. Such solid propellant compositions have been produced by mixing ammonium nitrate and liquid organic compounds that can be converted to solid organic polymeric fuels and then converting the hardenable mixtures so formed in suitably-shaped molds to produce solid propellants of the desired shape. The solid propellants so produced contain ammonium nitrate dispersed in a matrix of a solid organic polymer which thus functions as a binder for the ammonium nitrate as well as a fuel.

The above-described hardenable mixtures are often difficult to prepare, since ammonium nitrate is not readily wetted by various liquid organic compounds that can be converted to solid organic polymeric fuels. In addition, such known hardenable mixtures and the solid propellants produced therefrom suffer from one or more serious shortcomings. By way of illustration, the hardenable mixtures possess poor rheological properties in that they can not be readily introduced into molds (e.g., they do not pour readily). As a further illustration, the molded solid propellants produced from such hardenable mixtures oftentimes contain voids and are cracked, mechanically weak and disintegrate during storage owing to depolymerization of the organic polymeric fuels that form the matrices. As further illustration, the above-described solid propellants have fixed Specific Impulse values which limit the performance of the engines in which they are used and they have relatively high temperature sensitivities which necessitate their use in undesirably heavy engines.

It is an object of this invention to provide ammonium nitrate which has been so treated that hardenable mixtures containing the treated ammonium nitrate and liquid organic compounds that are convertible to solid organic polymeric fuels can be readily formed owing to the wetting of the treated ammonium nitrate by the liquid organic compound.

Other objects of this invention are to provide hardenable mixtures that are free of one or more of the above-described defects of the aforementioned known hardenable mixtures. More specifically, it is an object of this invention to provide hardenable mixtures that are convertible to solid propellants and that possess good rheological properties in that they can be readily poured into molds, good curing properties so that they can be cured to produce solid propellants that are free of voids and cracks, that are mechanically strong, and/or that are stable during storage.

Still another object of this invention is to provide ammonium nitrate which has been so treated that it imparts to solid propellants wherein it is incorporated increased Specific Impulse values and lower temperature sensitivities.

This invention provides ammonium nitrate coated with an organosiloxane comprising groups represented by the formula:



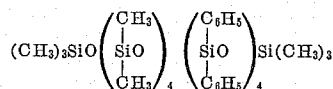
wherein R is a monovalent hydrocarbon group and n has

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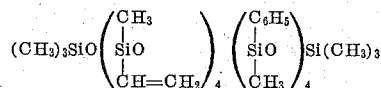
a value from 1 to 3 inclusive. This invention further provides hardenable mixtures containing the coated ammonium nitrate of this invention and a liquid organic compound that can be converted to solid organic polymeric fuel. This invention still further relates to solid propellant compositions produced from such hardenable mixtures and to processes for producing the coated ammonium nitrate, the hardenable mixtures and the solid propellant compositions of this invention.

Illustrative of the monovalent hydrocarbon groups represented by R in Formula 1 are the linear alkyl groups (for example the methyl, ethyl, propyl, butyl, and amyl groups), the cyclic alkyl groups (for example the cyclohexyl and cyclopentyl groups), the linear alkenyl groups (for example the vinyl and the allyl groups), the cyclic alkenyl groups (for example the cyclopentenyl and cyclohexenyl groups), the aryl groups (for example the phenyl and naphthyl groups), the alkaryl groups (for example the tolyl group), and the aralkyl groups (for example the benzyl and beta-phenylethyl groups). Preferably R represents a group containing from 1 to 10 carbon atoms inclusive.

The organosiloxane that forms the coating on the coated ammonium nitrate of this invention can be linear, cyclic, or cross-linked in structure. The linear organosiloxanes include those containing only groups represented by Formula 1 wherein n is 2 (e.g. hydroxyl and ethoxy end-blocked dimethylpolysiloxanes) $(HO[(CH_3)_2SiO]_xH$ and $C_2H_5O[(CH_3)_2SiO]_xC_2H_5$), as well as those containing only groups represented by Formula 1 wherein n is 3 (e.g., hexamethyl disiloxane). The linear organosiloxanes also include those containing both groups represented by Formula 1 wherein n is 2 and groups represented by Formula 1 wherein n is 3 [e.g., trimethylsiloxy end-blocked dimethylpolysiloxanes, $(CH_3)_3SiO[(CH_3)_2SiO]_xSi(CH_3)_3$]. The cyclic organosiloxanes contain only groups represented by Formula 1 wherein n is 2 (e.g., dimethylsiloxane cyclic trimer and tetramer). The cross-linked organosiloxanes are those containing groups represented by Formula 1, at least some of which are those wherein n has a value of 1 (e.g., methyl polysiloxane). In Formula 1 R can denote groups that can be the same or different on any given silicon atom or throughout a given organosiloxane molecule. Thus, suitable organosiloxanes include the compounds:



50 and



55 The coated ammonium nitrate of this invention can be produced by contacting ammonium nitrate with an organo(hydrocarboxy)silane having the formula:



60 wherein R and n have the above defined meanings in the presence of water to produce a siloxane comprising groups represented by Formula 1 on the surface of the ammonium nitrate.

Particularly preferred organo(hydrocarboxy)silanes are organotri(alkoxy)silanes represented more specifically by the formula:



70 wherein R' can be an ethyl, vinyl, amyl, or phenyl group and R'' is an alkyl group containing from 1 to 4 carbon atoms (e.g., a methyl, ethyl, propyl, or butyl group). More specifically, these preferred organotri(alkoxy)si-

lanes are ethyltrimethoxysilane, ethyltriethoxysilane, vinyltriethoxysilane, amyltriethoxysilane, and phenyltriethoxysilane. The organosiloxanes produced from these preferred organotri(alkoxy)silanes comprise groups represented by the formula:



wherein R' has the above-defined meaning. More specifically, these organosiloxanes are the ethylsiloxanes, vinylsiloxanes, amylsiloxanes, and phenylsiloxanes.

The organo(hydrocarbonoxy)silanes represented by Formula 2 are uniquely suited for use in the production of the coated ammonium nitrate of this invention. That is, although other hydrolyzable silanes (e.g., organohalosilanes) can be converted to organosiloxanes comprising groups represented by Formula 1, the coated ammonium nitrate produced with such other hydrolyzable silanes is not satisfactory (e.g., the coating does not adhere to the ammonium nitrate). Without wishing to be bound by any particular theory, it appears that the organosilanes represented by Formula 2 possess the ability to become properly oriented on the surface of the ammonium nitrate and so the organosiloxanes produced from the organo(hydrocarbonoxy)silanes may be mechanically locked on the surface of the ammonium nitrate owing to penetration into any irregularities on the surface and may be chemically linked to the surface of the ammonium nitrate (e.g., by hydrogen bonds). On the other hand, other hydrolyzable silanes (e.g., organohalosilanes) apparently do not possess the ability to become properly oriented on the surface of the ammonium nitrate and so coatings formed therefrom are not as securely bonded to the surface and readily separate therefrom.

The particular manner in which ammonium nitrate is treated with organo(hydrocarbonoxy)silanes in accordance with the process of this invention (i.e., treatment in the presence of water so that an organosiloxane is produced on the surface of the ammonium nitrate) is critical in providing coated ammonium nitrate possessing the improved properties set forth herein. Other methods of treating ammonium nitrate with organo(hydrocarbonoxy)silanes (e.g., contacting ammonium nitrate and an organo(hydrocarbonoxy)silane under anhydrous conditions) fails to produce the improvement in the properties of the ammonium nitrate such as are attained by the process of the invention.

In producing the coated ammonium nitrate of this invention, the ammonium nitrate can be brought into contact with the organo(hydrocarbonoxy)silane in the presence of water by any convenient method. By way of illustration, the organo(hydrocarbonoxy)silane can be vaporized and the vapor can be passed through a bed of ammonium nitrate. Preferably, however, the ammonium nitrate is brought into contact with the organo(hydrocarbonoxy)silane by forming a mixture of the ammonium nitrate and a solution containing the organo(hydrocarbonoxy)silane dissolved in a suitable solvent. The relative amount of ammonium nitrate and solution is not narrowly critical and so dispersions composed of relatively small amounts of ammonium nitrate dispersed in relatively large amounts of the solution can be employed. Preferably, however, the mixture is a paste composed of a relatively large amount of ammonium nitrate blended with a relatively small amount of the solution (e.g., from 10 to 90 parts by weight of the solution per 100 parts by weight of the ammonium nitrate). Such organo(hydrocarbonoxy)silane solutions can contain from 0.1 parts to 20 parts, or preferably from 0.5 part to 5 parts by weight of the organo(hydrocarbonoxy)silane per 100 parts by weight of a solvent. Suitable solvents are liquid organic compounds that dissolve the organo(hydrocarbonoxy)silanes and that are non-reactive with the organo(hydrocarbonoxy)silanes and ammonium nitrate. Suitable solvents include the aliphatic hydrocarbons (e.g.,

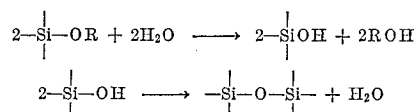
heptane and octane) and the aromatic hydrocarbons (e.g., benzene and toluene).

In producing the coated ammonium nitrate of this invention, it is essential that the organosiloxane comprising groups represented by Formula 1 is formed on the surface of the ammonium nitrate. If the organosiloxane is not formed on the surface of the ammonium nitrate, the organosiloxane will not adhere to the ammonium nitrate and a heterogeneous mixture of ammonium nitrate and the organosiloxane, rather than ammonium nitrate coated with the organosiloxane, is produced. By way of illustration, if a solution containing a preformed organosiloxane dissolved in one of the above-mentioned solvents is mixed with ammonium nitrate and the solvent is volatilized, there is produced a heterogeneous mixture of ammonium nitrate and the organosiloxane.

One method of insuring that the organosiloxane comprising groups represented by Formula 1 will be formed on the surface of the ammonium nitrate in producing the coated ammonium nitrate of this invention is by forming a mixture of ammonium nitrate and a solution containing an organo(hydrocarbonoxy)silane dissolved in a solvent of the above-described type and then bringing air that is laden with water vapor (e.g., air having a relative humidity of 40-90%) into contact with the mixture. The air can be at an elevated temperature so as to serve both as a means of bringing the water vapor into contact with the mixture and as a means for volatilizing the solvent.

Another method of insuring that the organosiloxane consisting essentially of groups represented by Formula 1 will be formed on the surface of the ammonium nitrate in producing the coated ammonium nitrate of this invention is by absorbing a small amount of water on the ammonium nitrate and then mixing the ammonium nitrate with a solution containing an organo(hydrocarbonoxy)silane dissolved in a solvent of the above-described type.

Hydrolysis and condensation reactions occur during the formation of the organosiloxane coating on the surface of the ammonium nitrate by the above-described methods. These reactions can be represented by the equations:



wherein R has the above defined meaning. These reactions occur spontaneously, even at temperatures below room temperature, but they are accelerated by elevated temperatures. More or less than the stoichiometric amount of water required by the above reactions can be employed. In the latter case, the organosiloxane contains silicon-bonded hydrocarbonoxy groups. The organosiloxanes can contain silicon-bonded hydroxyl groups owing to incomplete condensation thereof.

The temperature employed in either of the above-described methods of insuring that the organosiloxane comprising groups represented by Formula 1 will be formed on the surface of the ammonium nitrate in producing the coated ammonium nitrate of this invention is not narrowly critical. Thus, temperatures of from 0° C. to 150° C. are useful, but temperatures from 50° C. to 125° C. are preferred. Other temperatures can be used, but no commensurate advantage is gained thereby.

After the ammonium nitrate is coated with an organosiloxane comprising groups represented by Formula 1 as described above, it can be separated from any excess water, organo(hydrocarbonoxy)silane or from the solvent used in treating solution and from the alcohol (ROH) formed in the hydrolysis reaction by any suitable means (e.g., by filtration or by reducing the pressure over the system to volatilize the water, alcohol, organo(hydrocarbonoxy)silane, and/or solvent).

The amount of the organosiloxane in the coated ammonium nitrate of this invention is critical in order to produce satisfactory solid propellant compositions therefrom. The coated ammonium nitrate must contain at least 0.01 part but no more than 5.0 parts by weight (preferably from 0.1 part to 3.0 parts by weight) of the organosiloxane per 100 parts by weight of the ammonium nitrate. Lesser amounts of the organosiloxane coating result in incomplete coating of the ammonium nitrate, which in turn seriously impairs the rheological and molding properties of hardenable mixtures containing the coated ammonium nitrate and a liquid organic compound that can be converted to a solid organic polymeric fuel. Greater amounts of the organosiloxane coating seriously reduce the specific impulse values of solid propellant compositions. Ammonium nitrate having a particle size from 4 to 325 mesh (Standard Screen Size) is particularly useful. Although ammonium nitrate having other particle sizes can be used in solid propellant fuel compositions, no commensurate advantage is gained thereby.

When the coating on the coated ammonium nitrate of this invention is an amysiloxane or a vinylsiloxane, it has been unexpectedly found that the bulk density of the coated ammonium nitrate is greater than the bulk density of the uncoated ammonium nitrate from which it was produced. This surprising property of ammonium nitrate coated with amysiloxanes or vinylsiloxanes is a decided advantage since, by virtue of this property, more of the ammonium nitrate in the coated form can be introduced into a storage chamber of a given size. In addition, by virtue of this property, more of the ammonium nitrate in the coated form can be mixed with a liquid organic compound that can be converted to a solid organic polymeric fuel before loss of the continuous phase of the liquid organic compound occurs. This increase in bulk density is not observed in the case of ammonium nitrate having, for example, a methylsiloxane coating. The latter coated ammonium nitrates have bulk densities that are about the same as the bulk density of the uncoated ammonium nitrate from which they are produced.

The hardenable mixtures of the invention that are used to produce solid propellant compositions of this invention contain the coated ammonium nitrate of this invention and a liquid organic compound that can be converted to a solid organic polymeric fuel.

The liquid organic compounds that can be converted to solid organic polymeric fuels (i.e., the fuel which also serves as a binder) which are useful in hardenable mixtures of this invention include thermoplastic polymers that have been liquified by heat as well as liquid monomers and liquid partial polymers that can be cured to produce thermoplastic or thermoset solids (e.g., resins or elastomers). Such fuels are materials that are readily oxidized to liberate relatively large volumes of gas. Such liquid organic compounds include phenol-formaldehyde polymers that are in the "A" stage, asphalt, liquid thioether polymers, liquid urethane ether polymers, liquid partially cured alkyd resins, alkyl-substituted phenol-formaldehyde polymers that are in the "A" stage, aryl-substituted phenol-formaldehyde polymers that are in the "A" stage, liquid plasticized polyvinyl acetal compositions containing a sufficient amount of urea-formaldehyde or melamine-formaldehyde condensation product to make the composition thermo-setting, liquid melamine-formaldehyde condensation products, liquid substituted melamine-formaldehyde reaction products, and liquid alkyd-vinyl heteropolymers. Preferably, such liquid organic compounds have a viscosity from 500 to 10,000 centipoises at 25° C. to facilitate the incorporation of the coated ammonium perchlorate therein. Specific liquid organic compounds include an air blown asphalt that has a penetration with a 100 gram weight for four seconds at 77° F. of 12-20 and a softening point of 230° F.-240° F., tertiary-butyl phenol-formaldehyde polymer that are in the "A" stage, tertiary-amyl phenyl-formaldehyde polymers that are in the "A"

stage, alkyd-styrene heteropolymers that are in the "A" stage, alkyd-styrene heteropolymers, and the product of the alkaline-catalyzed condensation of one mole of phenol and two moles of formaldehyde having a viscosity of 1000 centipoises at 25° C. By a polymer that is in the "A" stage as employed herein is meant that the polymer is partially cured but is still liquid and capable of further curing.

The relative amount of the coated ammonium nitrate and the above-described liquid organic compound present in the hardenable mixtures of this invention can be varied widely, depending upon such factors as the particular liquid organic compound employed and the desired burning characteristics of the solid propellant composition produced from the hardenable mixture. Generally, from 30 parts to 125 parts by weight of the coated ammonium nitrate per 100 parts by weight of the liquid organic compound are useful. Although other relative amounts of these liquid organic compounds can be employed, no commensurate advantage is gained by employing such other amounts.

The hardenable mixtures of this invention can be produced by simply mixing the components together in any convenient sequence. In the case of liquid organic compounds that are hardened or solidified by curing, the mixing of the components of these hardenable mixtures is preferably conducted at room temperature to minimize any premature curing of the liquid organic compound. On the other hand, where the liquid organic compound is a polymer that is hardened or solidified by cooling (e.g., asphalt), the mixing is conducted at a temperature sufficiently elevated to maintain the polymer in the liquid state. If desired, various plasticizers (e.g., a toluene sulfonamide-formaldehyde reaction product) can be added to the mixtures to assist in obtaining thorough mixing of the components. The mixing can be accomplished in any suitable apparatus (e.g., sigma blade internal mixers). Owing to the improved properties of the coated ammonium nitrate of this invention, it is readily wetted by the liquid organic compounds and hence readily forms intimate mixtures therewith.

The hardenable mixtures of this invention can contain other ingredients in addition to the coated ammonium nitrate and the above-described liquid organic compounds. Such other ingredients can be added, for example, to accelerate the cure of those liquid organic compounds which are curable, to provide additional fuel, to improve even further the moldability of the hardenable mixtures and/or to improve even further the burning characteristics of the solid propellant composition produced from the hardenable mixtures. By way of illustration, compounds and mixtures of compounds such as chromium sesquioxide, ferrosioferic oxide, ZnO, Fe₃O₄, TiO₂, SnO₂, Al₂O₃, and CuO can be added to increase the burning rate of solid propellant composition produced from the hardenable mixtures. As a further illustration, metals and compounds, such as aluminum, lithium aluminum hydride, and ammonium picrate can be added to the hardenable mixtures to provide additional fuel.

The solid propellant compositions of this invention are produced by hardening the above-described hardenable mixtures of this invention. The method used to harden any particular mixture is dependent upon the type of liquid organic compound in the mixture. By way of illustration, when the liquid organic compound is normally solid thermoplastic resin (e.g., asphalt) which is in the liquid state because it was maintained at an elevated temperature above its melting point to allow for the incorporation of the coated ammonium nitrate therein, hardening can be accomplished simply by allowing the mixture to cool to room temperature. As a further illustration, when the liquid organic compound is an uncured or partially cured heat-curable compound that can be cured to form a normally solid thermoplastic resinous fuel the hardening can be accomplished by cur-

ing the liquid organic compound at elevated temperatures to form a liquid polymer and allowing the mixture to cool to room temperature. As a further illustration, when the liquid organic compound is an uncured or a partially cured compound that can be cured to form a solid thermoset resinous fuel, the hardening can be accomplished by simply curing the liquid organic compound to produce the resinous fuel. The hardening of the hardenable mixtures of this invention converts the mixtures into solid propellant compositions containing the coated ammonium nitrate of this invention dispersed in a matrix of a solid organic polymeric fuel.

The hardening of the hardenable mixtures of this invention is preferably performed after the hardenable mixture has been introduced into a mold that is designed to mold the mixture into the shape required by the configuration of the particular combustion chamber in which the solid propellant composition is to be employed. Owing to the usually excellent rheological properties of these hardenable mixtures, they can be generally readily introduced into such molds by any suitable means (e.g., by simple pouring or by pressure injection). Such excellent rheological properties are possessed by all of those mixtures wherein the coating on the ammonium nitrate is an organosiloxane composed of groups represented by Formula 4.

Curing of those hardenable mixtures of this invention which contain liquid organic compounds that are curable can be accomplished by any suitable means, which means are governed by the particular curable compound in the mixture. Some such curable mixtures can be cured simply by allowing them to stand at room temperature. Generally, however, it is desirable to accelerate the cure by heating the curable mixture. The particular temperature to which the curable mixture is heated to effect the cure will, of course, be dependent on the particular curable liquid organic compound in the mixture and on the presence or absence of a curing catalyst in the mixture. Cure temperatures from 60° C. to 150° C. are often suitable but other cure temperatures can be employed if desired.

The solid propellant compositions of this invention are generally free of voids and cracks and in addition they are usually mechanically strong and do not deteriorate on standing owing to the depolymerization of the solid organic polymer that serves as a fuel and a binder owing to any other cause. Such compositions usually have increased Specific Impulse values and lower temperature sensitivities as compared to otherwise identical compositions having uncoated ammonium nitrate. These advantageous properties are possessed by all of the solid propellant compositions of this invention wherein the coating on the ammonium nitrate is an organosiloxane composed of groups represented by Formula 4.

The solid propellant compositions of this invention can be treated in various conventional ways to improve their properties even further or to provide special effects. By way of illustration, a restrictive liner can be produced on the surfaces of the composition other than the surface which it is desired to burn in the combustion chamber of rocket engines in which it is to be employed. The restrictive liner insures that only the unlined surface burns.

The coated ammonium nitrate of this invention has been described above in connection with its use in producing, ultimately, solid propellant compositions. It should be noted, however, that the usefulness of the coated ammonium nitrate is not limited to such compositions, but rather, the coated ammonium nitrate can be employed in other applications (e.g., in blasting compositions and the like). In the latter applications, the coated ammonium nitrate need not be in particulate form, and other than the above-indicated amounts of the organosiloxane coating can be present per 100 parts of the ammonium nitrate.

The following examples illustrate the present invention.

Example 1

Ten grams of powdered ammonium nitrate (30 to 325 mesh) were suspended in 15 cubic centimeters of benzene in a 4-ounce glass jar. Vinyltriethoxysilane (0.2 gram) was added and the mixture ball milled with a dozen 0.5 inch diameter porcelain balls for 15 minutes. The balls were removed and the mixture transferred to an evaporating dish where the benzene was evaporated and the silane was hydrolyzed by passing air having a relative humidity of 60 percent over the dish. The coated ammonium nitrate so produced was heated to 100° C. for 10 minutes to remove the last traces of benzene. The ammonium nitrate so treated had a coating of a vinylsiloxane (i.e., a siloxane composed of $\text{CH}_2=\text{CHSiO}_{1.5}$ groups).

Example 2

One hundred grams of dry powdered ammonium nitrate (30 to 325 mesh) were stirred with 20 grams of vinyltriethoxysilane and 380 grams of benzene in a one gallon "Hobart" mixer to give a smooth paste. The material was spread out and exposed to the air having 50 percent relative humidity to permit the solvent to evaporate and to allow the vinyltriethoxysilane to hydrolyze on the surface of the ammonium nitrate. The treated material was then screened through a 30-mesh screen and baked at 100° C. for one hour to insure complete removal of all the benzene. A final screening through the 30-mesh screen completed the treatment process. The bulk density of the ammonium nitrate so treated was 0.945 gram per cubic centimeter, compared with 0.818 gram per cubic centimeter for similarly screened but untreated ammonium nitrate. The ammonium nitrate so treated had a coating of a vinylsiloxane (i.e., a siloxane composed of $\text{CH}_2=\text{CHSiO}_{1.5}$ groups).

When ammonium nitrate is treated in the manner described above with chlorosilanes as for example vinyltrichlorosilane, or with polysiloxanes as for example a dimethylpolysiloxane oil and the so-treated ammonium nitrate added to a partial polymer fuel, no advantages will be observed. That is to say, such admixtures are characterized by air pockets, bubbles, and are extremely difficult to cast and shape to any desired form. In addition, the resulting propellants will not be characterized by improved physical strengths.

Example 3

Ten grams of powdered ammonium nitrate (30 to 325 mesh) can be mixed with 0.2 gram of ethyltriethoxysilane that is dissolved in 5 grams of benzene to produce a paste. The paste so produced can be placed in an open dish and air that has been heated to 50° C. and that has a relative humidity of 50 percent can be passed over the dish to volatilize the benzene and to hydrolyze the silane. There is so produced ammonium nitrate that is coated with an ethylsiloxane (i.e., a siloxane composed of groups having the formula $\text{C}_2\text{H}_5\text{SiO}_{1.5}$) and that can be separated from any remaining benzene and the alcohol formed in the hydrolysis by heating at 100° C.

Example 4

Ten grams of powdered ammonium nitrate (30 to 325 mesh) can be mixed with 0.2 gram of amyltriethoxysilane that is dissolved in 5 grams of benzene to produce a paste. The paste so produced can be placed in an open dish and air that has been heated to 50° C. and that has a relative humidity of 50 percent can be passed over the dish to volatilize the benzene and to hydrolyze the silane. There is so produced ammonium nitrate that is coated with an amylsiloxane (i.e., a siloxane composed of groups having the formula $\text{C}_5\text{H}_{11}\text{SiO}_{1.5}$) and that can be separated from any remaining benzene and the alcohol formed in the hydrolysis by heating at 100° C.

Example 5

Ten grams of powdered ammonium nitrate (30 to 325 mesh) can be mixed with 0.2 gram of phenyltriethoxysilane that is dissolved in 5 grams of benzene to produce a paste. The paste so produced can be placed in an open dish and air that has been heated to 50° C. and that has a relative humidity of 50 percent can be passed over the dish to volatilize the benzene and to hydrolyze the silane. There is so produced ammonium nitrate that is coated with a phenylsiloxane (i.e., a siloxane composed of groups having the formula $C_6H_5SiO_{1.5}$) and that can be separated from any remaining benzene and the alcohol formed in the hydrolysis by heating at 100° C.

The siloxane coatings in the above examples are present in amounts from 0.01 part to 5.0 parts per 100 parts by weight of the ammonium nitrate.

Example 6

When 100 parts by weight of asphalt are melted, 50 parts by weight of ammonium nitrate coated with 0.5 part of a vinylsiloxane are mixed with the melted asphalt to produce a hardenable mixture and the mixture so formed is placed in a suitably shaped mold and is allowed to solidify by cooling, there is produced a solid propellant composition of this invention.

Example 7

Ten grams of powdered ammonium nitrate and a solution containing 0.2 gram of phenyltriethoxysilane and 0.2 gram of ethyltriethoxysilane that are dissolved in 5 grams of benzene can be blended to form a paste. That paste so formed can be placed in an open dish and air that has been heated to 50° C. and that has a relative humidity of 50% can be brought into contact with the paste (e.g., it can be passed over the dish) to hydrolyze the silanes and to volatilize the benzene. There is so produced ammonium nitrate that is coated with from 0.01 to 5.0 parts by weight per 100 parts by weight of the ammonium nitrate of a copolymeric organosiloxane composed of phenylsiloxo groups (i.e., $C_6H_5SiO_{1.5}$ groups) and ethylsiloxo groups (i.e., $C_2H_5SiO_{1.5}$ groups). The coated ammonium nitrate so produced can be separated from any remaining benzene and the alcohol formed in the hydrolysis of the silanes by heating at 100° C.

The latter example illustrates the production of ammonium nitrate coated with organosiloxanes composed of different types of siloxane groups represented by Formula 1. The production of ammonium nitrate having such coatings is accomplished by employing a mixture of suitable organo(hydrocarbonoxy)silanes represented by Formula 2 in the coating processes generally described above.

The "mesh" and the "Standard Screen Size" referred to herein have reference to particle size determined in accordance with the National Bureau of Standards Sieve Numbers.

What is claimed is:

1. Coated ammonium nitrate wherein the coating is an organosiloxane comprising groups represented by the formula:



wherein R is a monovalent hydrocarbon group and n has a value of 1.

2. Coated particulate ammonium nitrate wherein the coating is an organosiloxane consisting essentially of groups represented by the formula:



wherein R is a member selected from the group consisting of the ethyl, vinyl, amyl, and phenyl groups and wherein the coating is present in amount of from 0.1

part to 3.0 parts by weight per 100 parts by weight of the ammonium nitrate.

3. The coated ammonium nitrate of claim 2 wherein R is an ethyl group.

4. The coated ammonium nitrate of claim 2 wherein R is a vinyl group.

5. The coated ammonium nitrate of claim 2 wherein R is an amyl group.

6. The coated ammonium nitrate of claim 2 wherein R is a phenyl group.

7. The coated ammonium nitrate of claim 2 wherein the ammonium nitrate has a particle size from 4 to 325 mesh.

8. A hardenable mixture comprising particular ammonium nitrate that is coated with an organosiloxane comprising groups having the formula



wherein R is a monovalent hydrocarbon group and n has a value of 1, said coating being present in an amount from 0.1 to 3.0 parts by weight per 100 parts by weight of ammonium nitrate and a liquid organic compound that can be cured to form a solid organic polymeric fuel.

9. The hardenable mixture of claim 8 wherein the thermosetting liquid organic compound is asphalt.

10. The hardenable mixture of claim 8 wherein the liquid organic compound is a phenol-aldehyde polymer that is in the "A" stage.

11. The hardenable mixture of claim 8 wherein the liquid organic compound is liquid partially cured alkyd resin.

12. The hardenable mixture of claim 8 wherein the liquid organic compound has a viscosity from about 500 to about 10,000 centipoises at 25° C.

13. A hardenable mixture comprising particulate ammonium nitrate that is coated with an organosiloxane comprising groups having the formula:



wherein R' is a member selected from the group consisting of the ethyl, vinyl, amyl, and phenyl groups, said coating being present in an amount from 0.1 to 3.0 parts by weight per 100 parts by weight of ammonium nitrate; and a thermosetting liquid organic compound that can be cured to form a solid thermoset resinous fuel.

14. The hardenable mixture of claim 13 wherein R is an ethyl group.

15. The hardenable mixture of claim 13 wherein R is a vinyl group.

16. The hardenable mixture of claim 13 wherein R is an amyl group.

17. The hardenable mixture of claim 13 wherein R is a phenyl group.

18. A solid propellant composition comprising coated particulate ammonium nitrate that is coated with an organosiloxane comprising groups represented by the formula:



wherein R is a monovalent hydrocarbon group and n has a value of 1, said coating being present in an amount of from 0.1 to 3.0 parts by weight per 100 parts by weight of ammonium nitrate and a solid organic polymeric fuel which serves as a matrix for the coated particulate ammonium nitrate.

19. The solid propellant composition of claim 18 wherein the ammonium nitrate has a particle size of from 4 to 325 mesh.

20. The solid propellant composition of claim 18 wherein the solid organic polymeric fuel is asphalt.

21. The solid propellant composition of claim 18 wherein the solid organic polymeric fuel is a cured phenol-aldehyde polymer.

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22. The solid propellant composition of claim 18 wherein the solid organic polymeric fuel is a cured alkyl resin.

23. A solid propellant composition comprising coated particulate ammonium nitrate that is coated with an organosiloxane comprising groups represented by the formula:



wherein R is a member selected from the group consisting of the ethyl, vinyl, amyl, and phenyl groups, said coating being present in an amount of from 0.1 to 3.0 parts by weight per 100 parts by weight of ammonium nitrate; and a solid organic polymeric fuel which serves as a matrix for the coated particulate ammonium nitrate.

24. The solid propellant composition of claim 23 wherein R is an ethyl group.

25. The solid propellant composition of claim 23 wherein R is a vinyl group.

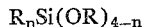
26. The solid propellant composition of claim 23 wherein R is an amyl group.

27. The solid propellant composition of claim 23 wherein R is a phenyl group.

28. A process for producing coated ammonium nitrate wherein the coating is an organosiloxane comprising groups represented by the formula:



wherein R is a monovalent hydrocarbon group and n has a value of 1, which comprises contacting ammonium nitrate with an organo(hydrocarboxy)silane having the formula:

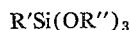


wherein R and n have the above-defined meanings, in the presence of water to produce said organosiloxane on the surface of the ammonium nitrate.

29. A process for producing coated ammonium nitrate wherein the coating is an organosiloxane comprising groups represented by the formula:

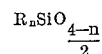


wherein R' is a member selected from the group consisting of the ethyl, vinyl, amyl, and phenyl groups, which comprises contacting ammonium nitrate with an organo(hydrocarboxy)silane having the formula:



wherein R' has the above-defined meaning and R'' is an alkyl group containing from 1 to 4 carbon atoms, in the presence of water to produce said organosiloxane on the surface of the ammonium nitrate.

30. A process for producing coated ammonium nitrate wherein the coating is an organosiloxane comprising groups represented by the formula:



wherein R is a monovalent hydrocarbon group and n has a value of 1, said process comprising forming a mixture of ammonium nitrate and a solution containing an organo(hydrocarboxy)silane having the formula:



wherein R and n have the above-defined meanings, that is dissolved in a liquid organic compound that is a solvent for the organo(hydrocarboxy)silane and that is non-reactive with the organo(hydrocarboxy)silane and ammonium nitrate; and bringing air that contains water vapor into contact with said mixture to produce the coated ammonium nitrate.

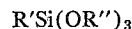
31. A process for producing coated ammonium nitrate

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wherein the coating is an organosiloxane comprising groups represented by the formula:

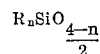


wherein R' is a member selected from the group consisting of the ethyl, vinyl, amyl, and phenyl groups, said process comprising forming a mixture of ammonium nitrate and a solution containing an organo(hydrocarboxy)silane that is represented by the formula:

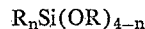


wherein R' has the above-defined meaning and R'' is an alkyl group containing from 1 to 4 carbon atoms which is dissolved in a liquid organic compound that is a solvent for the organo(hydrocarboxy)silane and that is non-reactive with the organo(hydrocarboxy)silane and ammonium nitrate; and bringing air that contains water vapor into contact with said mixture to produce the coated ammonium nitrate.

32. A process for producing coated ammonium nitrate wherein the coating is an organosiloxane comprising groups represented by the formula:



wherein R is a monovalent hydrocarbon group and n has a value of 1, said process comprising absorbing water on ammonium nitrate and forming a mixture containing the ammonium nitrate which has water absorbed thereon and a solution containing an organo(hydrocarboxy)silane represented by the formula:

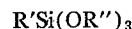


wherein R and n have the above-defined meanings that is dissolved in a liquid organic compound that is non-reactive with the organo(hydrocarboxy)silane and ammonium nitrate; and bringing air that contains water vapor into contact with said mixture to produce the coated ammonium nitrate.

33. A process for producing coated ammonium nitrate wherein the coating is an organosiloxane comprising groups represented by the formula:

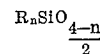


wherein R' is a member selected from the group consisting of the ethyl, vinyl, amyl, and phenyl groups, said process comprising absorbing water on ammonium nitrate and forming a mixture containing the ammonium nitrate which has water absorbed thereon and a solution containing an organo(hydrocarboxy)silane represented by the formula:



wherein R' has the above-defined meaning and R'' is an alkyl group containing from 1 to 4 carbon atoms that is dissolved in a liquid organic compound that is a solvent for the organo(hydrocarboxy)silane and that is non-reactive with the organo(hydrocarboxy)silane and ammonium nitrate; and bringing air that contains water vapor into contact with said mixture to produce the coated ammonium nitrate.

34. A process for producing a hardenable mixture that can be converted to a solid propellant composition, said process comprising forming a mixture containing coated particulate ammonium nitrate wherein the coating is an organosiloxane comprising groups represented by the formula:



wherein R is a monovalent hydrocarbon group and n has a value of 1, said organosiloxane being present in an amount of from 0.1 to 3.0 parts by weight per 100 parts by weight of ammonium nitrate; and a liquid organic compound that can be cured to form a solid organic polymeric fuel.

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35. A process for producing a hardenable mixture that can be converted to a solid propellant composition, said process comprising forming a mixture containing coated particulate ammonium nitrate wherein the coating is an organosiloxane comprising groups represented by the formula:



wherein R' is a member selected from the group consisting of the ethyl, vinyl, amyl, and phenyl groups, said organosiloxane being present in an amount of from 0.1 to 3.0 parts by weight per 100 parts by weight of ammonium nitrate, and a liquid organic compound that can be cured to form a solid organic polymeric fuel.

36. A process for producing solid propellant compositions, said process comprising hardening a mixture containing coated particulate ammonium nitrate wherein the coating is of an organosiloxane comprising groups represented by the formula:



wherein R is a monovalent hydrocarbon group and n has a value of 1, said organosiloxane being present in an amount of from 0.1 to 3.0 parts by weight per 100 parts by weight of ammonium nitrate, and a liquid organic compound that can be cured to form a solid organic polymeric fuel.

37. A process for producing solid propellant compositions, said process comprising hardening a mixture containing coated particulate ammonium nitrate wherein

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the coating is of an organosiloxane comprising groups represented by the formula:



wherein R is a member selected from the group consisting of the ethyl, vinyl, amyl, and phenyl groups, said organosiloxane being present in an amount of from 0.1 to 3.0 parts by weight per 100 parts by weight of ammonium nitrate, and a liquid organic compound that can be cured to form a solid organic polymeric fuel.

38. The process of claim 28 wherein the silane that is brought in contact with the ammonium nitrate is in the vapor phase.

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CARL D. QUARFORTH, *Primary Examiner.*

LEON D. ROSDOL, ROGER L. CAMPBELL,

Examiners.