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COATED AMMONIUM PERCHLORATE AND PROPELLANT COMPOSITIONS

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This invention relates to treated ammonium perchlorate and, more particularly, to organosiloxane-coated ammonium perchlorate.

Solid propellant compositions containing ammonium perchlorate 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 perchlorate 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 perchlorate dispersed in a matrix of a solid organic polymer which thus functions as a binder for the ammonium perchlorate as well as a fuel.

The above-described hardenable mixtures are often difficult to prepare, since ammonium perchlorate 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 the 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 perchlorate which has been so treated that hardenable mixtures containing the treated ammonium perchlorate and liquid organic compounds that are convertible to solid organic polymeric fuels can be readily formed owing to the wetting of the treated ammonium perchlorate 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 perchlorate which has been so treated that it imparts to solid propellants wherein it is incorporated increased Specific Impulse values and lower temperature sensitivities.

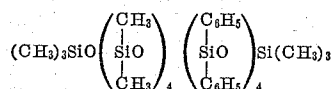
This invention provides ammonium perchlorate coated with an organosiloxane comprising groups represented by the formula:



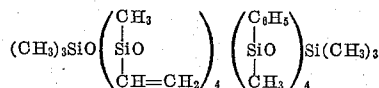
wherein R is a monovalent hydrocarbon group and n has a value from 1 to 3 inclusive. This invention further provides hardenable mixtures containing the coated ammonium perchlorate of this invention and a liquid organic compound that can be converted to solid organic polymeric fuel. This invention still further relates to solid propellant compositions produced from such hardenable mixtures and to processes for producing the coated ammonium perchlorate, 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 the 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).

The organosiloxane that forms the coating on the coated ammonium perchlorate 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 end-blocked dimethylpolysiloxanes, $HO[(CH_3)_2SiO]_xH$) 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 the same or different groups on the same silicon atom or throughout a given organosiloxane molecule. Thus, suitable organosiloxanes include the compounds:



and



The coated ammonium perchlorate of this invention can be produced by contacting ammonium perchlorate with an organohalosilane having the formula:



wherein R and n have the above defined meanings and X is a halogen atom (preferably chlorine) in the presence of water to produce a siloxane comprising groups represented by Formula 1 on the surface of the ammonium perchlorate.

The preferred organohalosilanes are organotrichlorosilanes represented more specifically by the formula:



wherein R' is a methyl, ethyl, vinyl, amyl, or phenyl group. More specifically, these preferred organotrichlorosilanes are methyltrichlorosilane, ethyltrichlorosilane, vinyltrichlorosilane, amyltrichlorosilane, and phenyltrichlorosilane. The organosiloxanes produced from

these preferred organotrihalosilanes comprise groups represented by the formula:



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

The organohalosilanes represented by Formula 2 are uniquely suited for use in the production of the coated ammonium perchlorate of this invention. That is, although other hydrolyzable silanes (e.g., organoalkoxysilanes) can be converted to organosiloxanes comprising groups represented by Formula 1, the coated ammonium perchlorate produced with such other hydrolyzable silanes is not satisfactory (e.g., the coating does not adhere to the ammonium perchlorate). 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 perchlorate and so the organosiloxanes produced from the organohalosilanes may be mechanically locked on the surface of the ammonium perchlorate owing to penetration into any irregularities on the surface and may be chemically linked to the surface of the ammonium perchlorate (such as by hydrogen bonds). On the other hand, other hydrolyzable silanes (e.g., organoalkoxysilanes) apparently do not possess the ability to become properly oriented on the surface of the ammonium perchlorate and so coatings formed therefrom are not as securely bonded to the surface and readily separate therefrom.

The particular manner in which ammonium perchlorate is treated with organohalosilanes 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 perchlorate) is critical in providing coated ammonium perchlorate possessing the improved properties set forth herein. Other methods of treating ammonium perchlorate with organohalosilanes (e.g., contacting ammonium perchlorate and an organohalosilane under anhydrous conditions) fail to produce the improvement in the properties of the ammonium perchlorate such as are attained by the process of the invention.

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

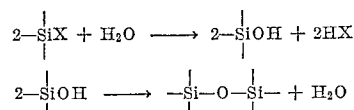
In producing the coated ammonium perchlorate of this invention, it is essential that the organosiloxane compris-

ing groups represented by Formula 1 is formed on the surface of the ammonium perchlorate. If the organosiloxane is not formed on the surface of the ammonium perchlorate, the organosiloxane will not adhere to the ammonium perchlorate and a heterogeneous mixture of ammonium perchlorate and the organosiloxane, rather than ammonium perchlorate 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 perchlorate and the solvent is volatilized, there is produced a heterogeneous mixture of ammonium perchlorate 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 perchlorate in producing the coated ammonium perchlorate of this invention is by forming a mixture of ammonium perchlorate and a solution containing an organohalosilane 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 perchlorate in producing the coated ammonium perchlorate of this invention is by absorbing a small amount of water on the ammonium perchlorate and then mixing the ammonium perchlorate with a solution containing an organohalosilane 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 perchlorate by the above-described methods. These reactions can be represented by the equations:



wherein X is a halogen atom. These reactions occur spontaneously, even at temperatures below room temperature, but they are accelerated by elevated temperatures.

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 perchlorate in producing the coated ammonium perchlorate 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 perchlorate is coated with an organosiloxane comprising groups represented by Formula 1 as described above, it can be separated from any excess water, organohalosilane or from the solvent used in treating solution and from the hydrogen halide (HX) 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, hydrogen halide, organotrichlorosilane, and/or solvent).

It is particularly desirable to remove the hydrogen halide from the coated ammonium perchlorate since the hydrogen halide may have a deleterious effect on the solid propellant compositions produced from the coated ammonium perchlorate (e.g., the hydrogen halide may promote the decomposition of the solid organic polymer that forms the matrix of the propellant composition).

One method is allowing the coated ammonium perchlorate

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to remain exposed to the atmosphere and to allow the hydrogen halide to volatilize.

The amount of the organosiloxane in the coated ammonium perchlorate of this invention is critical in order to produce satisfactory solid propellant compositions therefrom. The coated ammonium perchlorate 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 perchlorate. Lesser amounts of the organosiloxane coating result in incomplete coating of the ammonium perchlorate, which in turn seriously impairs the rheological and molding properties of hardenable mixtures containing the coated ammonium perchlorate 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 perchlorate having a particle size from 4 to 325 mesh (Standard Screen Size) is particularly useful. Although ammonium perchlorate 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 perchlorate of this invention is a methylsiloxane or a vinylsiloxane, it has been unexpectedly found that the bulk density of the coated ammonium perchlorate is greater than the bulk density of the uncoated ammonium perchlorate from which it was produced. This surprising property of ammonium perchlorate coated with methylsiloxanes or vinylsiloxanes is a decided advantage since, by virtue of this property, more of the ammonium perchlorate 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 perchlorate 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 perchlorate having, for example, an ethylsiloxane, an amylsiloxane, or a phenylsiloxane coating. The latter coated ammonium perchlorates have bulk densities that are about the same as the bulk density of the uncoated ammonium perchlorate 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 perchlorate of this invention and a liquid organic compound that can be converted to a solid organic polymeric fuel.

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 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 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 perchlorate of this invention, it is readily wetted by the liquid organic compounds and hence readily forms intimate mixtures therewith.

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 liquefied by heat as well as liquid monomer

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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 a urea-formaldehyde or melamine-formaldehyde condensation product to make the composition thermosetting, 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 50 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 polymers that are in the "A" stage, tertiary-amyl phenylformaldehyde polymers that are in the "A" stage, alkydstyrene heteropolymers that are in the "A" stage, alkyd-styrene heteropolymers, and the product of the alkaline-catalyzed condensations 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 perchlorate 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 perchlorate 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 contain other ingredients in addition to the coated ammonium perchlorate 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 hydrides, 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 a 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 perchlorate 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 curing 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 perchlorate 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 simply pouring or by pressure injection). Such excellent rheological properties are possessed by all of those mixtures wherein the coating on the ammonium perchlorate 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 or owing to any other cause. Such compositions often have increased Specific Impulse values and lower temperature sensitivities as compared to otherwise identical compositions wherein the ammonium perchlorate is uncoated. These advantageous properties are possessed by all of the solid propellant compositions of this invention wherein the coating on the ammonium perchlorate 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 surface 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 perchlorate 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 perchlorate is not limited to such compositions, but rather, the coated ammonium perchlorate can be employed in other applications (e.g., in blasting compositions and the like). In the latter applications,

the coated ammonium perchlorate 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 perchlorate.

The following examples illustrate the present invention.

Example 1

Eight grams of finely divided ammonium perchlorate having a particle size of 30 to 350 mesh were stirred with 3.2 grams of a solution containing 5 parts by weight of vinyltrichlorosilane dissolved in 100 parts by weight of toluene to provide 2 parts by weight of vinyltrichlorosilane per 100 parts by weight of the ammonium perchlorate. The wet paste which was formed was well stirred and transferred to an evaporating dish where it was allowed to stand exposed to air at 40–50% relative humidity for one hour. During this interval the toluene evaporated and the vinyltrichlorosilane became hydrolyzed to deposit a coating of vinylsiloxane (i.e., a siloxane composed of $\text{CH}_2=\text{CHSiO}_{1.5}$ groups) on the ammonium perchlorate. After the one hour period, tests made with pH test paper showed no acidity (i.e., no HCl) was present. The last traces of toluene were removed by placing the material in a vacuum desiccator and evacuating to 2 to 3 millimeters of mercury pressure for 30 minutes. Coated ammonium perchlorate so produced was a free-flowing powder as compared to the non-flowing original NH_4ClO_4 and it contained about 0.3 part by weight of the vinylsiloxane per 100 parts by weight of the ammonium perchlorate.

Example 2

This was a repetition of the above example except that 98 grams of ammonium perchlorate were treated with a solution of 2 grams of vinyltrichlorosilane in 38 grams of toluene. On this larger scale the procedure was as before until it came to complete removal of the toluene after completion of the hydrolysis step. The material was heated for 30 minutes at 100° C. before vacuum drying in order to finally remove the last traces of the toluene. The treated material was then found to be identical with that produced before.

Example 3

Nine hundred eighty grams of ammonium perchlorate having a particle size of 30 to 350 mesh were treated with a solution of 20 grams of vinyltrichlorosilane in 380 grams of toluene. The mixing was carried out in a large evaporating dish, using a stirrer having a large "Teflon" blade. A slow stream of air at 40% relative humidity was passed over the mixture while it was stirred to evaporate the toluene and hydrolyze the vinyltrichlorosilane. After it became reasonably dry, the material was allowed to stand in the dish without continuous stirring, but being agitated occasionally with a spatula until all signs of acidity (i.e., HCl) had disappeared, about 30 minutes. After this interval, the material was screened through a 30 mesh screen and heated for 30 minutes at 100° C. in an air circulating oven, and then allowed to cool in a vacuum desiccator at 2 to 3 millimeters of mercury pressure. The treated material was a fine, very mobile powder which produced clouds of dust when moved, and which splashed like water when shaken. The bulk density was measured and found to be 1.408 grams per cubic centimeter compared with 1.087 grams per cubic centimeter for untreated material, an increase of 37%. Analysis of the coated ammonium perchlorate showed that it contained 0.18 part of the vinylsiloxane coating per 100 parts by weight of the ammonium perchlorate.

Example 4

This example is identical with Example 3 except that 20 grams of methyltrichlorosilane were used in place of 20 grams of vinyltrichlorosilane, and the amount of toluene reduced to 300 grams to reduce the evaporation time. The final material was again a very mobile powder

with a bulk density of 1.389 grams per cubic centimeter. Analysis showed that a coating of 0.34 part of the methylsiloxane (i.e., a siloxane composed of $\text{CH}_3\text{SiO}_{1.5}$ groups) per 100 parts by weight of the ammonium perchlorate had been produced on the ammonium perchlorate.

Example 5

When ammonium perchlorate was coated with an ethylsiloxane (i.e., a siloxane composed of $\text{C}_2\text{H}_5\text{SiO}_{1.5}$ groups), the coated ammonium perchlorate was found to have a bulk density of 1.360 grams per cubic centimeter.

Example 6

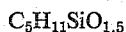
This example is identical with Example 4 with the exception that 20 grams of phenyltrichlorosilane were used in place of the methyltrichlorosilane. The final material was less free-flowing and contained many lumps which were then crushed in a mortar. The bulk density was very close to that of untreated ammonium perchlorate, namely 1.0755 grams per cubic centimeter. Analysis showed 1.0 part of phenylsiloxane (i.e., a siloxane composed of $\text{C}_6\text{H}_5\text{SiO}_{1.5}$ groups) coating per 100 parts by weight of the ammonium perchlorate.

Example 7

When 100 parts by weight of asphalt are melted, 50 parts by weight of ammonium perchlorate 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 8

This example is also identical with Example 4 except that 20 grams of amyltrichlorosilane were used in place of 20 grams of methyltrichlorosilane. This material showed less tendency to compact than the material described in Example 5 but had a lower bulk density, 1.064 grams per cubic centimeter. Analysis showed 0.7 part of a coating of amylsiloxane (i.e., a siloxane composed of



groups) per 100 parts by weight of the ammonium perchlorate.

When samples of ammonium perchlorate which had been treated with the chlorosilanes in the manner described in the above examples are added to a partial polymer which when cured serves as a fuel in a solid propellant, it is noted that the rheological properties of the admixture are excellent. That is to say, the hardenable mixture obtained is free of voids and air pockets, readily flows, and can be cast or shaped as desired. In addition, such mixtures, when cured to a solid state, will be characterized by stability during storage and by improved physical properties. On the other hand, untreated ammonium perchlorate, when added to a liquid partial polymer which when cured serves as a fuel and binder for solid propellants produces a mixture that possesses poor rheological and molding properties. That is to say, thorough admixtures of the uncoated ammonium perchlorate and partial polymers are difficult to obtain and, moreover, that the mixtures are of high viscosity and are difficult to mold or shape. The physical properties of solid propellants prepared from untreated ammonium perchlorate are characterized by instability during storage and by poor physical properties.

When ammonium perchlorate is treated with organoalkoxysilanes (as for example vinyltriethoxysilane) and preformed organosiloxanes (as for example a dimethylsiloxane oil) in the manner described above and subsequently mixed with partial polymer fuels, the resulting admixture is also characterized by poor rheological properties. In addition, little or no improvement is obtained in the stability and physical properties of solid propellants prepared from ammonium perchlorate so coated.

Example 9

Ten grams of powdered ammonium perchlorate and a solution containing 0.2 gram of phenyltrichlorosilane and 0.2 gram of ethyltrichlorosilane that are dissolved in 5 grams of benzene can be blended to form a paste. The 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 perchlorate that is coated with from 0.1 to 3.0 parts by weight per 100 parts by weight of the ammonium perchlorate of a copolymeric organosiloxane composed of phenylsiloxy groups (i.e., $\text{C}_6\text{H}_5\text{SiO}_{1.5}$ groups) and ethylsiloxy groups (i.e., $\text{C}_2\text{H}_5\text{SiO}_{1.5}$ groups). The coated ammonium perchlorate so produced is separated from any remaining benzene and the hydrogen chloride formed in the hydrolysis of the silanes by heating at 100° C.

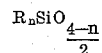
The latter example illustrates the production of ammonium perchlorate coated with organosiloxanes composed of different types of siloxane groups represented by Formula 1. The production of ammonium perchlorate having such coatings is accomplished by employing a mixture of suitable organohalosilanes represented by Formula 2 in the coating process generally described above.

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

Each monovalent hydrocarbon group represented by R in Formula 1 desirably contains from 1 to 10 carbon atoms.

What is claimed is:

1. Coated ammonium perchlorate 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 perchlorate 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 methyl, 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 perchlorate.

3. The coated ammonium perchlorate of claim 2 wherein R is a methyl group.

4. The coated ammonium perchlorate of claim 2 wherein R is an ethyl group.

5. The coated ammonium perchlorate of claim 2 wherein R is a vinyl group.

6. The coated ammonium perchlorate of claim 2 wherein R is an amyl group.

7. The coated ammonium perchlorate of claim 2 wherein R is a phenyl group.

8. The coated ammonium perchlorate of claim 2 wherein the ammonium perchlorate has a particle size from 40 to 350 mesh.

9. A hardenable mixture comprising particulate ammonium perchlorate 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 perchlorate and a liquid organic com-

pound that can be cured to form a solid organic polymeric fuel.

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

11. The hardenable mixture of claim 9 wherein the liquid organic compound is a phenol-aldehyde polymer that is in the "A" stage.

12. The hardenable mixture of claim 9 wherein the liquid organic compound is liquid partially cured alkyd resin.

13. The hardenable mixture of claim 9 wherein the liquid organic compound has a viscosity from about 500 to about 10,000 centipoises at 25° C.

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



wherein R' is a member selected from the group consisting of the methyl, 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 perchlorate; and a thermosetting liquid organic compound that can be cured to form a solid thermoset resinous fuel.

15. The hardenable mixture of claim 14 wherein R is a methyl group.

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

17. The hardenable mixture of claim 14 wherein R is a vinyl group.

18. The hardenable mixture of claim 14 wherein R is an amyl group.

19. The hardenable mixture of claim 14 wherein R is a phenyl group.

20. A solid propellant composition comprising coated particulate ammonium perchlorate 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 perchlorate and a solid organic polymeric fuel which serves as a matrix for the coated particulate ammonium perchlorate.

21. The solid propellant composition of claim 20 wherein the ammonium perchlorate has a particle size of from 40 to 350 mesh.

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

23. The solid propellant composition of claim 20 wherein the solid organic polymeric fuel is a cured phenol-aldehyde polymer.

24. The solid propellant composition of claim 20 wherein the solid organic polymeric fuel is a cured alkyd resin.

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



wherein R is a member selected from the group consisting of methyl, 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 perchlorate; and a solid organic polymeric fuel which serves as a matrix for the coated particulate ammonium perchlorate.

26. The solid propellant composition of claim 25 wherein R is a methyl group.

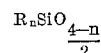
27. The solid propellant composition of claim 25 wherein R is an ethyl group.

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

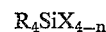
29. The solid propellant composition of claim 25 wherein R is an amyl group.

30. The solid propellant composition of claim 25 wherein R is a phenyl group.

31. A process for producing coated ammonium perchlorate 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 perchlorate with an organohalosilane having the formula:



wherein R and n have the above-defined meanings and X is a halogen atom, in the presence of water to produce said organosiloxane on the surface of the ammonium perchlorate.

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

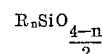


wherein R' is a member selected from the group consisting of methyl, ethyl, vinyl, amyl, and phenyl groups, which comprises contacting ammonium perchlorate with an organohalosilane having the formula:

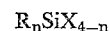


wherein R' has the above-defined meaning, in the presence of water to produce said organosiloxane on the surface of the ammonium perchlorate.

33. A process for producing coated ammonium perchlorate 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 perchlorate and a solution containing an organohalosilane that is represented by the formula:



wherein R and n have the above-defined meanings and X is a halogen atom that is dissolved in a liquid organic compound that is a solvent for the organohalosilane and that is nonreactive with the organohalosilane and ammonium perchlorate; and bringing air that contains water vapor into contact with said mixture to produce the coated ammonium perchlorate.

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



wherein R' is a member selected from the group consisting of methyl, ethyl, vinyl, amyl, and phenyl groups, said process comprising forming a mixture of ammonium perchlorate and a solution containing an organohalosilane that is represented by the formula:



wherein R' has the above-defined meaning which is dissolved in a liquid organic compound that is a solvent for the organohalosilane and that is non-reactive with the organohalosilane and ammonium perchlorate; and bringing air that contains water vapor into contact with said mixture to produce the coated ammonium perchlorate.

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35. A process for producing coated ammonium perchlorate 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 perchlorate and forming a mixture containing the ammonium perchlorate which has water absorbed thereon and a solution containing an organohalosilane represented by the formula:



wherein R and n have the above-defined meanings and X is a halogen atom that is dissolved in a liquid organic compound that is non-reactive with the organohalosilane and ammonium perchlorate; and bringing air that contains water vapor into contact with said mixture to produce the coated ammonium perchlorate.

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



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



wherein R' has the above-defined meaning that is dissolved in a liquid organic compound that is a solvent for the organohalosilane and that is non-reactive with the organohalosilane and ammonium perchlorate; and bringing air that contains water vapor into contact with said mixture to produce the coated ammonium perchlorate.

37. 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 perchlorate 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 perchlorate; and a liquid organic compound that can be cured to form a solid organic polymeric fuel.

38. 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 perchlorate wherein the coating is

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an organosiloxane comprising groups represented by the formula:



wherein R' is a member selected from the group consisting of methyl, 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 perchlorate, and a liquid organic compound that can be cured to form a solid organic polymeric fuel.

39. A process for producing solid propellant compositions, said process comprising hardening a mixture containing coated particulate ammonium perchlorate 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 perchlorate, and a liquid organic compound that can be cured to form a solid organic polymeric fuel.

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



wherein R is a member selected from the group consisting of methyl, 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 perchlorate, and a liquid organic compound that can be cured to form a solid organic polymeric fuel.

41. The process of claim 32 wherein the silane that is brought in contact with the ammonium perchlorate is in the vapor phase.

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