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CASTABLE AMMONIUM PERCHLORATE PROPELLANT COMPOSITIONS

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This invention relates to ammonium perchlorate compositions and especially ammonium perchlorate explosives and propellants which can be safely handled in a liquid, semi-liquid or pasty state. More particularly it relates to castable and hardenable ammonium perchlorate compositions containing organoureido compounds and to explosive or propellant compositions obtained therefrom as well as processes for preparation thereof.

Ammonium perchlorate is widely used in commerce, especially as a component in explosives and rocket propellants. This material is difficult to cast into desired shapes, especially for explosives and propellants, since it does not exhibit a melting point. When heated to increasily higher temperatures at atmospheric pressure, it will suddenly deflagrate without previous indication of melting between 300° C. and 400° C. depending on the heating rate.

When ammonium perchlorate is employed in explosives and propellants, it is generally the oxidizing agent and a combustible material, such as a combustible organic material, is generally also employed. In order to obtain proper stoichiometry between ammonium perchlorate oxidizer and combustible material in a rocket propellant, the ammonium perchlorate should comprise at least 75 weight percent of the ammonim perchlorate-combustible material mixture.

Ammonium perchlorate mixtures with combustible organic materials previously have been produced by mixing powdered ammonium perchlorate and powdered combustible organic material and filling the powdery mixture under slight compression into suitable containers or cartridges. This procedure is satisfactory for blasting charges of a relatively low charge density. In rocket propellants, however, such mixtures cannot be employed because the finished rocket propellant must be free of voids and air enclosures which would cause an unequal buring rate or even detonation. A powdery mixture is incapable of being packed in such form as to completely eliminate voids and air spaces. For this reason, rocket propellants must be introduced into the rocket motor in liquid form, free of air bubbles, and must then be solidified in place. Even when the combustible material is employed in a liquid form, the resulting mixtures are very stiff and thixotropic. Such non-flowing pastes were difficult to handle and could be cast or molded only by applying pressure and/or vibrating devices in order to obtain a uniform filling of a simple mold. Even then voids and air bubbles will not be completely avoided. Attempts were made to improve the situation by the addition of wetting agents, such as lecithin, fatty acid monoglycerides or resin acid monoglycerides, to the ammonium perchlorate-combustible material mixture, but these additives resulted only in slight improvement in the rheological properties.

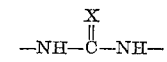
It is therefore a principal object of the invention to prepare castable ammonium perchlorate compositions.

It is a further object to prepare ammonium perchlorate-combustible material compositions which can be solidified to a void-free state.

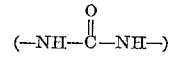
Still a further object is to prepare improved ammonium perchlorate-containing rocket propellants.

I have now found that a mixture of ammonium perchlorate and an organoureido compound wherein the molar ratio of organoureido compound/ammonium perchlorate is from about 0.4 to about 5.0 has a melting point below about 100° C. This mixture can be easily melted and casted in liquid form into suitable molds to form void-free solid ammonium perchlorate containing compositions. It can also be easily mixed in its molten form with liquid combustible materials to form a hardenable mixture which is then cast into molds to form void-free ammonium perchlorate explosives and rocket propellants. The presence of the organoureido compound in the final propellant composition does not impair the buring rate or other properties of the propellant composition. When the organoureido compound/ammonium perchlorate molar ratio is between about 0.4 and about 3.0 the molten mixture is turbid and consists of suspensions of ammonium perchlorate in the molten composition. This composition is still quite castable. When the organoureido compound/ammonium perchlorate molar ratio is between about 3.0 and about 5.0, the molten mixture is clear.

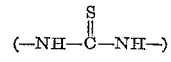
The organoureido compounds useful in this invention are those materials containing the functional structure



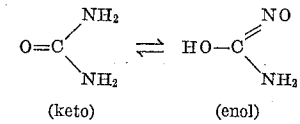
wherein X is selected from the class consisting of oxygen and sulfur. The expression "ureido" as used herein thus refers to both "ureido"



and "thioureido"



compounds. Examples of such useful compounds are: urea, thiourea, hydantoin, monoethylol dimethylhydantoin, 2-thiohydantoin (glycolylthiourea), allantoin (5-ureidohydantoin), alloxane (mesoxalyl urea), parabanic acid (oxalyl urea), barbituric acid (malonyl urea), maleyl urea, uric acid and the like. It is preferred that the organoureido compounds of the type described above have a melting point in the pure state of less than about 150° C. It is also preferred that the organoureido compounds have two allotropic modifications, such as the keto and enol forms found in urea. This is illustrated by the following equation:



(keto) (enol)

The melting points of organoureido compound-ammonium perchlorate mixtures can further be appreciably depressed by the addition of lithium perchlorate. The eutectic temperature of the binary system urea-ammonium perchlorate of 91° C. is further depressed in the ternary system urea-ammonium perchlorate-lithium perchlorate to about 20° C. Such mixtures are liquid at room temperature and stay liquid for an indefinite period of time if kept under anhydrous conditions. This invention thus transforms an unmeltable ammonium perchlorate into a liquid that remains liquid even at room temperature. The amount of lithium perchlorate required is about 12 to about 20 mole percent based on total moles of am-

monium perchlorate, organoureido compound and lithium perchlorate.

The liquid organic combustible compounds that can be converted to solid organic polymeric fuels (i.e., the fuel which also serves as a binder for the ammonium perchlorate-combustible material mixture) which are useful in hardenable mixtures of this invention include thermoplastic polymers that have been liquefied by heat as well as liquid monomer 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 combustible compounds include aldehyde condensation polymers, such as phenol-formaldehyde, phenol-acetaldehyde, phenol-furfural, cresol-formaldehyde, urea-formaldehyde, melamine-formaldehyde polymers and the like. Preferably these polymers are in the "A" stage. The expression "A" stage as used herein refers to a polymer that is partially cured but is still liquid and capable of further curing. Alkyl and aryl substituted aldehyde condensation polymers can also be employed. The terms "curable," "cured" and "curing" as used in this application are intended to mean the formation of a substantially solid polymer by means of molecular interaction rather than merely cooling to below solidification temperature.

Further examples of liquid combustible materials used in hardenable compositions of the present invention are unsaturated polyester resins. Such resins are generally composed of the reaction products of maleic anhydride, phthalic anhydride or fumaric acid and ethylene glycol, diethylene glycol or propylene glycol which has been diluted with from 10 to 40 weight percent of monomeric styrene, as well as the corresponding alcohol- acid- and oil-modified products. Such materials can also be employed in the "A" stage.

Still further examples of liquid combustible materials are the epoxy-type resins which comprise, for example, the glycidyl ethers of polyhydric phenols as well as blends of such diglycidyl ethers of polyhydric phenols with such modifying ingredients as the polyphenol compounds. Other useful epoxy resins include derivatives of cyclohexene epoxide; for example, 3,4-epoxy-6-methylcyclohexylmethyl - 3,4-epoxy-6-methylcyclohexanecarboxylate, 1-epoxyethyl-3,4-epoxycyclohexane, dicyclopentadiene dioxide and the like. Such materials can also be employed in the "A" stage.

Additional examples of useful liquid organic combustible materials are: asphalt, liquid thioether polymers, liquid urethane ether polymers, liquid partially cured alkyd resins, liquid plasticized polyvinyl acetal compositions containing a sufficient amount of a urea-formaldehyde or melamine-formaldehyde condensation product to make the composition thermosetting, liquid alkyd-vinyl heteropolymers, alkyd-styrene heteropolymers, polyethylene, polypropylene, polystyrene, acrylic resins, vinyl resins, buna rubber, butadiene polymers, isoprene, butadiene-isobutylene copolymers, polychloroprene, polyisobutylene and the like.

It is preferred that the liquid organic combustible material have a viscosity from 50 to 10,000 centipoises at 25° C. to facilitate blending with the liquid ammonium perchlorate-organoureido compound composition.

The hardenable mixtures of this invention can contain other ingredients in addition to the ammonium perchlorate-organoureido compound composition 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 the burning characteristics of the solid propellant composition produced from the novel hardenable mixtures. By way of illustration, compounds and mixtures of compounds such as chromium sesquioxide, ferrosoferric oxide, ZnO, Fe_3O_4, TiO_2, SnO_2, Al_2O_3 and CuO can be added to increase the burning rate of solid propellant compositions 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 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 (e.g., resins or elastomers), the mixing of the components of these hardenable mixtures is preferably conducted at temperatures below the curing temperature 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 mixture to assist in obtaining thorough mixing of the components. The mixing can be accomplished in any suitable apparatus.

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, 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 ammonium perchlorate-organoureido castable compositions of this invention dispersed in a matrix of a solid organic polymeric fuel.

The hardening of the hardenable mixture 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 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 ammonium perchlorate is mixed and combined with an organoureido compound as described above.

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. Curing catalysts, such as metal salts (tin octoate and the like) can also be used to accelerate the cure. The particular temperature to which the curable mixture is heated to effect the cure will, of course, be dependent on the particular curable liquid or-

ganic 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.

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. Such liner is placed on a surface other than the composition surface which is desired to burn in the combustion chamber of rocket engines in which such composition is to be employed. The restrictive liner insures that only the unlined surface burns.

The ammonium perchlorate-organoureido castable and hardenable compositions of this invention have been described above primarily in connection with their use in producing, ultimately, solid propellant compositions. It should be noted, however, that the usefulness of the castable ammonium perchlorate-organoureido compositions is not limited to such compositions, but rather such castable ammonium perchlorate-organoureido compositions can be employed in other applications, such as blasting compositions and the like.

The following examples illustrate the present invention.

EXAMPLE 1

Various mixtures of urea and ammonium perchlorate were heated to determine their melting points. The results are shown in the following Table I.

Table I

EUTECTIC MELTING POINTS OF THE BINARY SYSTEM AMMONIUM PERCHLORATE-UREA

Moles Urea	Moles NH_4ClO_4	Molar Ratio, Urea/ NH_4ClO_4	Melting Point, ° C.
0.25	1	0.25	--------
0.25	0.75	0.33	Pasty at 150° C.
0.50	1	0.5	90
1	1	1.0	91
1.5	1	1.5	91
2	1	2.0	91
3	1	3.0	92
4	1	4.0	92
9	1	9.0	103
9.5	0.5	19.0	117

It can be seen from the above data that an ammonium perchlorate organoureido composition having an organoureido/ammonium perchlorate molar ratio of about 0.4 to about 5.0 has a significantly reduced melting point.

EXAMPLE 2

Various mixtures of urea, ammonium perchlorate and lithium perchlorate were heated to determine their melting points. The results are shown in the following Table II.

Table II

EUTECTIC MELTING POINTS OF THE TERNARY SYSTEM UREA-AMMONIUM PERCHLORATE-LITHIUM PERCHLORATE

Moles Urea	Moles NH_4ClO_4	Moles $LiClO_4$	Molar Ratio, Urea/ NH_4ClO_4	Mole-Percent $LiClO_4$	Melting Point, ° C.
1	1	0.3	1	13	20
1	1	0.4	1	16.6	60
1	1	0.5	1	20	84
1	1.5	0.4	0.67	13.8	73
0.67	1.1	0.3	0.61	14.6	75

It can be seen from the above data that an ammonium perchlorate-organoureido composition containing about 12 to about 20 mole percent lithium perchlorate has a still further reduced melting point.

EXAMPLE 3

An ammonium perchlorate-urea-lithium perchlorate composition was melted and added at 80° C. to a liquid organic combustible material. The liquid mixture was easily cast into molds and subsequently solidified by heating to 80° C. for 20 hours. The overall mixture had the composition of:

	Percent by weight
Urea	23.2
Ammonium perchlorate	45.5
Lithium perchlorate	12.0
Combustible binder	19.3

The binder consisted of a composition of:

	Percent by weight
6 - methyl - 3,4 - epoxycyclohexylmethyl-6-methyl-3,4-epoxycyclohexane carboxylate, marketed under the name Unox 201 Epoxy by the Union Carbide Corporation	41.1
Polypropylene glycol	38.0
Tallow monoglyceride	12.95
Maleic anhydride	7.07
Tin octoate containing 28 percent by weight Sn (curing catalyst)	0.88

The ammonium perchlorate composition had an organoureido-ammonium perchlorate molar ratio of about 1.

EXAMPLE 4

A mixture consisting of 19 percent by weight urea, 74.4 percent by weight ammonium perchlorate and 6.6 percent by weight polyethylene wax was easily melted at 120–125° C. (the melting range of the polyethylene wax) and cast into molds. The mixture becomes solid when cooled to room temperature. This mixture had an organoureido/ammonium perchlorate molar ratio of about 0.5.

EXAMPLE 5

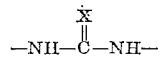
A mixture of 16 percent by weight urea, 64 percent by weight ammonium perchlorate (organoureido/ammonium perchlorate molar ratio of about 0.49) and 20 percent by weight organic combustible material as described in Example 3 above was easily melted together and cast into a mold and subsequently solidified by heating to 80° C. for 20 hours.

EXAMPLE 6

A mixture was obtained consisting of 12 percent by weight urea, 60 percent by weight ammonium perchlorate (organoureido/ammonium perchlorate molar ratio of about 0.4), 17.2 percent by weight unsaturated polyester resin (reaction product of polyether and maleic anhydride), 2.4 percent by weight 6-methyl-3,4-epoxycyclohexylmethyl - 6-methyl-3,4-epoxycyclohexane carboxylate, marketed under the name Unox 201 Epoxy by the Union Carbide Corporation, 0.4 percent by weight tin octoate (curing catalyst) and 8.0 percent by weight aluminum powder (additional fuel). This mixture forms a viscous but castable liquid at 80–90° C. It can be mixed in any heatable mixing machine. In this case it is advantageous to keep the tin octoate catalyst out during the main mixing procedure and to add it only during the last minutes of mixing before discharging the mixer in order to avoid premature polymerization or gelation of the mass in the mixing machine. All other mixtures described in Examples 3 through 6 can be treated in the same mechanical manner without danger of ignition or explosion. The above described mixture containing curing catalyst solidifies at 90° C. within 30 minutes.

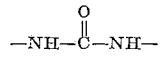
What is claimed is:

1. A hardenable and castable ammonium perchlorate composition comprising (1) ammonium perchlorate, (2) an organoureido compound containing the functional group

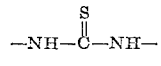


wherein X is selected from the class consisting of oxygen and sulfur and wherein the organoureido/ammonium perchlorate molar ratio is from about 0.4 to about 5.0, and (3) a liquid organic combustible material that can be converted to a solid organic polymeric fuel.

2. A hardenable and castable ammonium perchlorate composition as claimed in claim 1 wherein the organoureido compound contains the group



3. A hardenable and castable ammonium perchlorate compositions claimed in claim 1 wherein the organoureido compound contains the group



4. A hardenable and castable ammonium perchlorate composition as claimed in claim 1 wherein the organoureido compound is urea.

5. A hardenable and castable ammonium perchlorate composition as claimed in claim 1 wherein the ammonium perchlorate is present in an amount of at least 75 weight percent based on total weight of ammonium perchlorate and combustible organic material.

6. A hardenable and castable ammonium perchlorate composition as claimed in claim 1 wherein the liquid organic combustible material is hardenable by curing.

7. A hardenable and castable ammonium perchlorate composition as claimed in claim 1 wherein the liquid organic combustible material is a mixture of 6-methyl-3,4 - epoxycyclohexyl - methyl-6-methyl-3,4-epoxycyclohexane carboxylate, polypropylene glycol, tallow monoglyceride, and maleic anhydride.

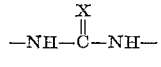
8. A hardenable and castable ammonium perchlorate composition as claimed in claim 1 wherein the liquid organic combustible material is polyethylene wax.

9. A hardenable and castable ammonium perchlorate composition as claimed in claim 1 wherein the liquid organic combustible material is a mixture of an unsaturated polyester resin and 6-methyl-3,4-epoxycyclohexylmethyl-6-methyl-3,4-epoxycyclohexane carboxylate.

10. A hardenable and castable ammonium perchlorate composition as claimed in claim 1 which contains in addition lithium perchlorate.

11. A hardenable and castable ammonium perchlorate composition as claimed in claim 10 wherein the lithium perchlorate is present in an amount of about 12 to about 20 molar percent based on total moles of ammonium perchlorate, organoureido compound and lithium perchlorate.

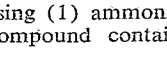
12. A solid propellant composition comprising the solidified form of an ammonium perchlorate composition comprising (1) ammonium perchlorate, (2) an organoureido compound containing the functional group



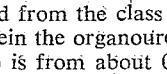
wherein X is selected from the class consisting of oxygen and sulfur and wherein the organoureido/ammonium perchlorate molar ratio is from about 0.4 to about 5.0, and (3) a liquid organic combustible material that can be converted to a solid organic polymeric fuel.

13. A solid propellant composition as claimed in claim

12 wherein the organoureido compound contains the group



14. A solid propellant composition as claimed in claim 12 wherein the organoureido compound contains the group



15. A solid propellant composition as claimed in claim 12 wherein the organoureido compound is urea.

16. A solid propellant composition as claimed in claim 12 wherein the ammonium perchlorate is present in an amount of at least 75 weight percent based on total weight of ammonium perchlorate and combustible organic material.

17. A solid propellant composition as claimed in claim 12 wherein the organic combustible material was solidified by curing.

18. A solid propellant composition as claimed in claim 12 wherein the organic combustible material is a mixture of 6 - methyl - 3,4 - epoxycyclohexylmethyl-6-methyl-3,4-epoxycyclohexane carboxylate, polypropylene glycol, tallow monoglyceride and maleic anhydride.

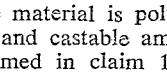
19. A solid propellant composition as claim in claim 12 wherein the organic combustible material is polyethylene wax.

20. A solid propellant composition as claimed in claim 12 wherein the organic combustible material is a mixture of an unsaturated polyester resin and 6-methyl-3,4-epoxycyclohexylmethy-6-methyl-3,4-epoxycyclohexane carboxylate.

21. A solid propellant composition as claimed in claim 12 which contains in addition lithium perchlorate.

22. A solid propellant composition as claimed in claim 12 wherein the lithium perchlorate is present in an amount of about 12 to about 20 molar percent based on total moles of ammonium perchlorate, organoureido compound and lithium perchlorate.

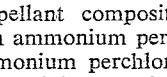
23. A castable ammonium perchlorate composition comprising a mixture of ammonium perchlorate, lithium perchlorate, and an organoureido compound containing the functional group



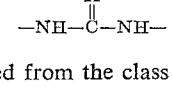
where X is selected from the class consisting of oxygen and sulfur, and wherein the organoureido/ammonium perchlorate molar ratio is from about 0.4 to about 5.0.

24. A castable ammonium perchlorate composition as claimed in claim 23 wherein the lithium perchlorate is present in an amount of about 12 to about 20 molar percent based on the total moles of ammonium perchlorate, organoureido compound and lithium perchlorate.

25. A castable ammonium perchlorate composition as claimed in claim 23 wherein the organoureido compound contains the group



26. A castable ammonium perchlorate composition as claimed in claim 23 wherein the organoureido compound contains the group



27. A castable ammonium perchlorate composition as claimed in claim 23 wherein the organoureido compound is urea.

28. A hardenable and castable ammonium perchlorate

composition comprising (1) ammonium perchlorate, (2) an organoureido compound selected from the class consisting of urea, thiourea, hydantoin, monomethylol dimethylhydantoin, 2-thio-hydantoin, allantoin, alloxane, parbanic acid, barbituric acid, maleyl urea and uric acid, and (3) a liquid organic combustible material that can be converted to a solid organic polymeric fuel, the organoureido compound and ammonium perchlorate being present in a molar ratio of from about 0.4 to about 5.0.

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