United States Patent Office 3,551,222 Patented Dec. 29, 1970

3,551,222

COATED WATER SOLUBLE INORGANIC OXIDIZERS

Martin H. Kaufman, John D. O'Drobinak, and John W. Carroz, China Lake, Calif., assignors to the United States of America as represented by the Secretary of the Navy

No Drawing. Filed Mar. 6, 1967, Ser. No. 621,732
Int. Cl. C06b 19/02
U.S. Cl. 149—7 10 Claims

ABSTRACT OF THE DISCLOSURE

Ammonium perchlorate, potassium perchlorate and potassium nitrate coated with a silane or chrome complex for use in composite propellant formulations whereby improved bonding between the binder and oxidizer results in greatly increased elongations.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The present invention relates to coated water soluble inorganic oxidizers and, more particularly, to ammonium perchlorate, potassium perchlorate and potassium nitrate coated with a silane or chrome complex.

In the solid propellant field composite propellant compositions containing an inorganic oxidizer and a polymeric binder as a fuel are among the types employed to supply thrust for rocket engines. Improved oxydizer-binder systems are of primary concern. The present invention is for an improved propellant oxidizer-binder system wherein the binder-solids adhesive strength is about as strong as the cured binder cohesive strength.

It is therefore an object of the present invention to provide a coated inorganic oxidizer for use in composite rocket propellant formulations.

Another object is to provide a coated inorganic oxidizer which when used in propellant formulations aids in reducing the environmental effect of humidity on the long range physical properties of the propellant grain.

Yet another object is to provide a simple method for coating water soluble oxidizer ingredients for use in pyrotechnics, explosives and propellants.

Still another object is to provide an oxidizer-binder system wherein improved bonding between the binder and oxidizer results in increased propellant elongations.

Other objects, features and many of the attendant advantages of this invention will become readily appreicated as the same become better understood by reference to the following detailed description.

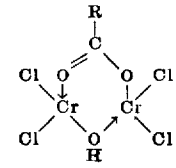
In accordance with the present invention silane or chrome complexes diluted with water and hydrolyzed with ammonium hydroxide and a weighed amount of the water soluble oxidizers selected from the group consisting of ammonium perchlorate, potassium perchlorate and potassium nitrate were thoroughly mixed together. The resulting mixture was dried in a hot air stream at 190–210° F. The hot air stream keeps the inorganic oxidizer particles essentially separate from each other and provides a very rapid evaporation of the water and/or other diluent such as alcohol. The dry coated oxidizer was then heated for from 16–20 hours in an oven maintained at 85 to 100° C. to assure complete polymerization of the coating around the individual oxidizer crystals. The coating present is in an amount ranging from 0.025 to 1.0 part by weight per 100 parts by weight inorganic oxidizer. When the coated oxidizer was blended into a hydrocarbon binder, carboxyterminated polybutadiene (CTPB) in

this instance, curing of the propellant was not affected, nor did aging appear to affect the effectiveness of the coating. The physical properties of the propellant were improved due to the coated oxidizer because of improved adhesion between the binder and the oxidizer.

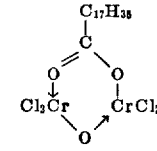
The nature or mechanism of the present process is not known. The silane and chrome complexes were found to contain groupings which were widely different in polarity. One of the groupings was found to be very polar so as to promote adhesion to the ionic ammonium perchlorate and the other grouping was very similar to the binder molecular structure used in the composite propellant system. It is known that ammonium perchlorate is ionic and on drying holds on to the last trace of water tenaciously. Now, since the properties of water result from its hydroxyl (—OH) components, it was hypothesized that one end of the coating complex or agent should also be a hydroxyl, and the other end would be mainly hydrocarbon. If a different binder type were used, the coating complex would be different in order to conform to the binder.

Two similar materials which were found to have the required structures were alkyloxy silanes and Werner type chrome complexes. The pertinent reactions of both are quite similar, i.e., hydrolysis to hydroxyl groups followed by polymerization on heating.

The chrome complexes are best represented as follows:

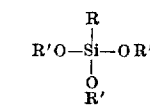


wherein R is a radical derived from an organic acid selected from the group consisting of gallic, sorbic, linoleic, methyacrylic, cyanoacetic, stearic and myristic. The Werner-type chromium complexes of carboxylic acids used herein were developed from the reaction products of chromyl chloride and various organic acids. Typical complexes are the "Quilon" chrome complexes, a registered trade name product comprising for example, a chromium complex of stearic acid having the formula



and "Volan" another registered trade name product comprising the chromium complex of methycrylic acid. The chemistry of chromium complexes, methods of manufacture, application and various uses are discussed in Advances in Chemistry Series (1959), No. 23, "Chromium Complexes" by F. B. Hauserman, pages 338–356.

The alkyloxy silanes are represented by the following formula

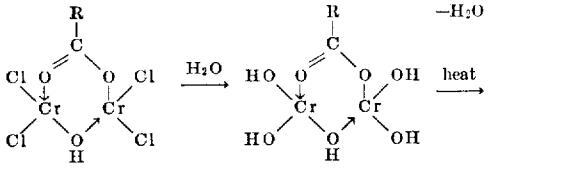


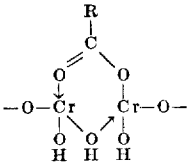
wherein R' is an alkyl group and R represents a large number of long chain radicals or groups. The silanes used herein are known commercially as Silane 4086 which is 3,4-epoxycyclohexyltrimethoxysilane and Silane 1100 which is aminopropyltriethoxysilane.

The structure of R is only limited by practical synthetic techniques and may be represented by an extremely large number of groups or structures. In the case of the chrome

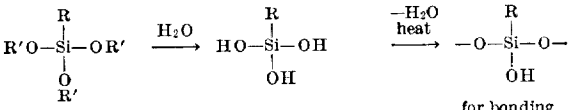
complexes they represent any group alpha to a carboxylic acid.

Under similar conditions the chromium complexes and the silanes used herein hydrolyze and on heating polymerize. The general reaction is shown as follows:





for bonding to AP



for bonding to AP

The coating solutions contain about 5 to 30% solids. The actual coatings range from 0.025–0.25% of the ammonium perchlorate.

The coating complex does not appear to affect propellant cure. Table I below illustrates the effect of the chrome complex on propellant cure.

TABLE I.—THE EFFECT OF COATING AGENT CONCENTRATION ON PROPELLANT CURE RATE

Concentration sorbate chrome complex, percent	Modulus, p.s.i. (10 percent)	Tensile strength, p.s.i.	Elongation at maximum tensile, percent	Elongation at rupture, percent	Gel after 10 days at 180° F., percent
0	1,079	108	12	17	74
0.08	1,019	103	12	14	76
0.17	955	99	25	26	73
0.33	1,105	112	20	23	77
0.50	1,052	108	30	32	74

Aging does not appear to affect the effectiveness of the coating. Table II below using Volan M for a coating, which is the chromium complex of methacrylic acid, gives some experimental data on aging characteristics.

TABLE II.—THE EFFECT OF AGING ON COATING EFFECTIVENESS

Aged at 180° F., weeks	0	1	2	3
Tensile strength of control, p.s.i.	163	168	170	179
Tensile strength of coated, p.s.i.	160	169	179	183
Elongation of control, percent	8.2	7.1	6.5	5.2
Elongation of coated, percent	14.0	11.5	11.0	9.0

The effectiveness of ammonium perchlorate (AP) coated with silane or chrome complexes in an unoptimized composite propellant was examined. The physical property data are tabulated in Table III. The propellant used consisted of carboxyterminated polybutadiene polymer and an imine curative. The formulations were cured for one week at 135° F.

TABLE III.—EFFECTIVENESS OF VARIOUS SIDE CHAIN STRUCTURES FOR BONDING AP TO CTPB

Coating agent	Concentration, grams soln/100 g. AP	Molecules 10%, p.s.i.	Tensile strength, p.s.i.	Elongation at maximum TS, percent	Elongation at rupture, percent
Control		2,080	94	13	16
Volan E[a]	0.5	1,940ρ	97	29	3
Volan H	0.5	1,760	87	30	35
Volan Z	0.5	1,960	96	26ρ	35
Volan Zρ	0.73	2,070	95	32	30
Volan M	0.5	1,810	94	25	28
Volan M	0.73	2,000	92	28	38
Volan X	0.5	2,420	102	23	22
Volan X	0.73	1,930	90	27	37
Quilon S	0.5	1,920	92	20	21
Quilon S	0.73	1,630	86.5	22.5	24
Quilon M	0.5	2,300	96	20	28
Quilon M	0.73	1,670	83	24	36
Silane 4086[b]	0.5	2,720	103	29	30
Silane 1100[c]	0.5	2,660	104	23	32

[a] Letter designate chain on the chromyl complex derived from organic acid:
Volan E=Gallic.
Volan H=Sorbic.
Volan Z=Linoleic.
Volan M=Methacrylic.
Volan X=Cyanoacetic.
Quilon S=Stearic.
Quilon M=Myristic.
[b] 3,4-epoxycyclohexyltrimethoxysilane.
[c] Aminopropyltriethoxysilane.

The effects of increased propellant solids loading and high temperature aging (180° F.) on the adhesion properties were determined by using Volan E coated AP as a representative example (Table IV). Data shows that the coating is effective at solids loadings of 85% as well as 80% and that it remains effective under high temperature aging even though the binder used in the propellants degrades.

TABLE IV.—EFFECT OF 85% SOLIDS LOADING AND HIGH TEMPERATURE AGING ON PROPELLANTS UTILIZING COATED AP (HX-868 CURE)

Coating agent	Percent 400μ AP	Percent 200μ AP	Modulus, p.s.i.	Tensile maximum, p.s.i.	Percent elongation at maximum tensile	Weeks at 180° F.
Control (none)	20.4	47.6	2,840	111	10.0	0
			3,270	128	8.0	1
			4,800	133	5.4	3
Volan E	20.4	47.6	2,170	119	35.0	0
			3,180	146	20.0	1
			4,120	165	9.8	3

Physical properties were determined at different temperatures on propellants which contained either coated or uncoated AP. The data shows effective adhesion at +77° F. and +165° F. There is the possibility that cohesive failure occurred in the binder at −65° F. (Table V).

TABLE V.—COATING EFFECTIVENESS ON PROPELLANT PHYSICAL PROPERTIES MEASURED AT DIFFERENT TEMPERATURE (HX-868 CURE)

Coating	Test temperature, ° F.	Modulus, p.s.i.	Tensile, maximum, p.s.i.	Percent elongation at maximum tensile	Percent elongation at rupture
Control	+165	2,100	110	9	10.0
	+77	2,320	131	14	14.3
	−65	16,310	582	6	6.8
Volan E	+165	1,800	107	19	20.8
	+77	2,360	124	35	35.0
	−65	17,510	523	6	6.6

To gain further evidence that the bond between the oxidizer and the binder was strengthened samples of Volan E coated ammonium perchlorate crystals and uncoated ammonium perchlorate crystals were placed into the binder side by side. The material was then cured. The cured material was then stressed using an Instron tensile machine and periodic photographs were taken. They showed that the binder pulled away (dewetting) from the uncoated ammonium perchlorate crystals, but the bond between the Volan E coated ammonium perchlorate crystals and the binder remained intact.

The following Table VI gives the coating effectiveness on propellant physical properties wherein the coating was Volan E and the oxidizers were potassium perchlorate and potassium nitrate.

TABLE VI.—COATING EFFECTIVENESS ON PROPELLANT PHYSICAL PROPERTIES (THE PROPELLANT CONSISTED ESSENTIALLY OF 20% BINDER, 16% ALUMINUM AND 64% OXIDIZER)

Coating	Modulus (p.s.i.)	Tensile (p.s.i.)	Elongation (percent)
Control (No coating)	6,700	163	4
Volan E coated potassium nitrate	6,300	194	9.2
Control (No coating)	5,080	144	5.6
Volan E coated potassium perchlorate	4,640	183	9.9

TABLE VII.—EFFECT OF HYDROLYSIS VARIABLES ON PHYSICAL PROPERTIES

Solution, AP contact time, hours	AP saturated water in coating solution, cc.	Modulus, (10%), p.s.i.	Tensile strength, p.s.i.	Elongation at maximum tensile, percent
23	20	1,250	81	42
23	40	1,240	82	33
0.25	20	1,320	82	36
0.25	40	1,170	82	42
Control		1,320	81	18

Within the limits of the test, variation in contact time has broad limits, as well as volume of water used per gram of ammonium perchlorate (AP).

In order to determine whether or not the AP saturated solution was affecting the AP particle size distribution a screen analysis was run on random samples of both coated and uncoated AP (Table VII).

TABLE VIII.—SCREEN ANALYSIS OF COATED AND UNCOATED AP

AP	Mean diameter (μ)	90% point (μ)	90% range (μ)
Control	203	280	175
Volan E coated	199	295	212
Control	433	517	198
Volan E coated	433	520	205

The data indicates negligible alteration of the particle size distributions for the AP that was tested.

By this invention the elongations of composite propellants have significantly increased without appreciable lessening of tensile strength. Through improved propellant elongations by means of the coated inorganic oxidizers, ammonium perchlorate, potassium perchlorate and potassium nitrate it is now possible to achieve higher loadings while still maintaining acceptable physical properties. In addition strength may be improved while still maintaining acceptable elongation.

The technique of application and of drying the coating complex on the oxidizer particles is critical and involves careful controls. The complex was diluted with a small quantity of water or alcohol, then hydrolyzed with dilute ammonium hydroxide. Additional water and/or alcohol was added to raise the volume of the solution to just wet the amount of ammonium perchlorate to be coated. The solution was then added to the ammonium perchlorate which was then thoroughly mixed with a soft spatula. The next step was to dry the product. Two procedures were used: (1) glass rotary evaporation and (2) hot air stream (fluidized bed). The latter gives consistently good results.

In the rotary evaporator the ammonium perchlorate very often stuck to the glass wall, moreover, particle-particle contact prior to hard cure of the agent may actually rub off the coating.

In the fluidized bed a hot (190–210° F.) air stream keeps the oxidizer particles essentially separate from each other and provides a very rapid evaporation of the water and/or alcohol.

In order to insure complete polymerization of the coating around the individual oxidizer particles the freshly dried materials were heated for at least 16 hours in an oven maintained at 85 to 100° C. Results using the fluidized drying technique are presented in Table VI below. The coating materials and process used were as follows:

(1) 3.00 g. Volan H
(2) 20 or 40 ml. of AP saturated water
(3) Addition of 6.6 g. of 1% NH_4OH with rapid stirring
(4) Pour resulting solution onto 600 g. of AP and mix with a soft spatula
(5) Dry in fluidized bed for 10 minutes at 190° F.
(6) Post dry in steam oven for 18 hours at 190° F.

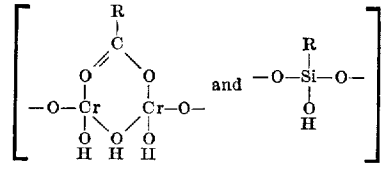
Humidity is detrimental to composite propellant grains due mainly to the presence of the water soluble oxidizers. In the present invention the hydrocarbon chain on the coating complex will no doubt act as an effective barrier to water molecules. The coating agents, acting as a barrier between the oxidizer and binder, will probably also eliminate the deleterious effects of the oxidizer on the overall curing and aging process.

Although the process described herein produces a single coating on a water soluble crystal of a silane or chrome complex, coating the cured crystals with yet another layer of the same complex or another complex can be achieved by the same procedure. For example, ammonium perchlorate coated with a chrome complex may then be coated with the silane complex and cured. It is probable that the double coating may effect improved characteristics such as water impermeability.

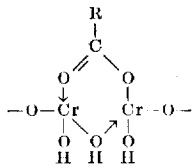
Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. Coated inorganic oxidizers selected from the group consisting of ammonium perchlorate, potassium perchlorate and potassium nitrate, wherein the coating is a chromium complex selected from the group represented by



and



wherein R is a radical derived from a member selected from the group of organic acids consisting of gallic, sorbic, linoleic, stearic, methacrylic, cyanoacetic and myristic and wherein the coating is present in an amount ranging from 0.025 to 1 part by weight per 100 parts by weight inorganic oxidizer.

2. The product of claim 1 wherein oxidizer is ammonium perchlorate and the coating is the chromium complex of methacrylic acid.

3. The product of claim 2 wherein the coating is the chromium complex of gallic acid.

4. The product of claim 2 wherein the coating is the chromium complex of sorbic acid.

5. The product of claim 2 wherein the coating is the chromium complex of linoleic acid.

6. The product of claim 2 wherein the coating is the chromium complex of cyanoacetic acid.

7. The product of claim 2 wherein the coating is the chromium complex of stearic acid.

8. The product of claim 2 wherein the coating is the chromium complex of myristic acid.

9. The product of claim 1 wherein the oxidizer is potassium perchlorate and the coating is the chromium complex of gallic acid.

10. The product of claim 1 wherein the oxidizer is potassium nitrate and the coating is the chromium complex of gallic acid.

References Cited

UNITED STATES PATENTS

3,058,858	10/1962	Batchelder et al.	149—19
3,190,775	6/1965	Ender	149—7X
3,190,776	6/1965	Ender	149—7X

LELAND A. SEBASTIAN, Primary Examiner

U.S. Cl. X.R.

149—61, 76, 83; 264—3