

1

3,701,697

**PRESSURE COMPENSATED PYROTECHNIC
TIME DELAY COMPOSITION**

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10 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a pyrotechnic time delay composition which comprises tungsten, potassium perchlorate, barium chromate, diatomaceous earth, and a metal fluoride selected from the group consisting of magnesium fluoride, ceric fluoride, strontium fluoride, and calcium fluoride.

BACKGROUND OF THE INVENTION

Compressed columns of solid powder mixtures have long been used for initiating some desired pyrotechnic result, at the end of a predetermined time delay period. The earliest form of such pyrotechnic device consisted of a confined column of black powder which could be ignited at one end so that the flame and glow front could advance along the column to the other end at a substantially uniform and predetermined rate.

So called "delay mixtures" have been developed consisting of powdered manganese, silicon, boron, and zirconium nickel alloys in combination with solid oxidizers, such as barium chromate, lead chromate, and potassium perchlorate. Many of these existing type "delay mixtures" are subject to a number of serious limitations. Very often the range of burning time per lineal inch is restricted to a narrow range, i.e. 10-13 seconds. Many are subject to undesirable variations in burning rate responsive to changes in pressure and temperature. Many are not ignitable in a rarified atmosphere or, at least, do not burn consistently under such conditions. In addition, very often the electrical conductivity of the mixture, both before and after the pyrotechnic reaction, is low, and this is undesirable when the delay train is to be used in multi-stage rockets and similar modern applications.

In an effort to overcome these disadvantages Olander, in Letters Patent No. 3,028,229 formulated pyrotechnic time delay compositions which were easily ignitable, were consistently burning, were chemically stable, were supposedly relatively unaffected by temperature and pressure, had a broad range of burning times and were electrically conductive. Olander achieved these results by combining either chromium, molybdenum or tungsten with potassium perchlorate and a second oxidizer, such as barium chromate; with the quantity of potassium perchlorate being less than the stoichiometric equivalent of the metal powder present in the mixture.

Olander used chromium and molybdenum mixtures to produce compositions which have a burning rate between about one and about ten seconds per inch. Tungsten was used to form compositions with a burning rate of about 40 seconds per inch. However, the tungsten compositions of Olander do not produce a burning rate of over 40 seconds per inch and for many purposes a slower burning

2

rate would be desirable. For example, when one is presented with space limitations but still desires a considerable time delay, one can decrease the column length if one can also decrease the burning rate. Changing of the concentration or the particle size of the metal has been used as a standard method for burning rate control of tungsten powders. However, with decreasing tungsten concentration or increasing particle size of the metal, the ignitability of the system is reduced. Therefore, attempts to obtain compositions burning slower than 40 seconds per inch have been unsuccessful. Furthermore, even with the addition of siliceous matter, such as diatomaceous earth, for a beneficial effect on the control of compaction and upon the reproducibility of the burning rate, the pyrotechnic time delay composition of Olander has the disadvantage that its burning rate is effected by increases in pressure above atmospheric.

SUMMARY OF THE INVENTION

It is an object of this invention to produce pyrotechnic time delay compositions which have all of the desired properties of previously known compositions, and, in addition, which produce a slower burning rate than said compositions.

These and other objectives are accomplished by incorporating up to about 5 percent of a chemically inert material such as calcium fluoride, magnesium fluoride, ceric fluoride or strontium fluoride into tungsten containing compositions.

**DESCRIPTION OF THE PREFERRED
EMBODIMENTS**

Investigations on the combustion of tungsten delay powders have shown that oxidation of tungsten at the boundary between unreacted and reacted material is a rate controlling factor in the burning process. From these results a new method to obtain slow burning compositions has been derived; i.e. by the formation of a molten layer on the surface of tungsten during burning. While this can be accomplished by raising the burning temperature above the melting point of tungsten trioxide, it is preferably accomplished by incorporating a low melting material into the composition. The low melting material must be chemically inert and must have a melting point below the burning temperature of the pyrotechnic composition. Some of the suitable materials, which can be used are either calcium fluoride, magnesium fluoride, ceric fluoride, strontium fluoride, or mixtures thereof. It is preferred to use calcium fluoride.

The compositions of the instant invention contain potassium perchlorate as a primary oxidizer, tungsten, diatomaceous earth, barium chromate as a secondary oxidizer and a low melting material. Up to 5 percent of the fluoride, based on the weight of the composition, can be incorporated into any of the tungsten compositions of U.S. Pat. No. 3,028,229. Generally, the amount of powdered or finely divided tungsten can vary from about 10-90 percent by weight of the composition, and the amount of tungsten present will determine the time of burning. The amount of potassium perchlorate varies from about 4.5 to about 15 percent, with the proviso that the quantity of potassium perchlorate is less than the stoichiometric equivalent of tungsten powder present in the mixture. The amount of barium chromate, which acts as a reaction modifier to slow the burning rate, will

3

vary from about 10 to about 60 percent. The amount of diatomaceous earth will vary from about 0 to about 12 percent by weight of the composition. An especially desirable composition will contain 3 percent of diatomaceous earth and 3 percent of calcium fluoride. If the entire amount of diatomaceous earth present in the compositions of Olander is replaced by 5 percent of calcium fluoride, loading characteristics become worse and consolidation of the powder in the delay test vehicle becomes difficult. However, such a composition, while not preferred, is still within the scope of this invention. Thus, it is generally preferred to have from about 3 to about 12 percent of diatomaceous earth present. The following compositions are exemplary of the many combinations which may be made without departing from the principle of our invention.

EXAMPLE I

	Percent by wt.
Powdered metallic tungsten, 4 micron	24
Finely divided barium chromate	60
Finely divided potassium perchlorate	10
Finely ground diatomaceous earth	3
Calcium fluoride	3

The above composition was prepared according to Schedule A, set forth hereinafter, and dried at 200° F. for a minimum of 8 hours. The batches used were limited in production size, i.e. 2000 to 12,000 grams. The compositions were preblended in 1 gallon capacity glass jars by rolling on a jar rolling mill for about 15 minutes. The amount of material in a jar never exceeded 3000 grams. Mulling was done in a Simpson mix-muller for 30 minutes, with scraping down every 10 minutes for the 12,000 gram batches and in a Lancaster mixer for 15 minutes for the 2000 and 2500 gram batches. The composition was then forced through a 30 mesh USS sieve and dried for a minimum of 24 hours at 140° F. before loading and test firing.

Schedule A

Ingredients:	Preparation
Tungsten	—325 mesh USS sieve.
Barium chromate	—30 mesh USS sieve.
Potassium perchlorate	—100+200 mesh USS sieve.
Diatomaceous earth	—20 mesh USS sieve.
Calcium fluoride	—100 mesh USS sieve.

The resulting composition, in a vented system, had a burning time of 47.508 seconds/inch at 71° F.

EXAMPLE II

The composition of Example I was altered, in that a composition was formulated containing 25% tungsten and 59% barium chromate (with the other ingredients remaining constant). The composition had a burning time at 71° F. of 43.1814 seconds/inch.

EXAMPLE III

The composition of Example I was altered in that a composition was formulated containing 32% tungsten and 52% barium chromate, with the other ingredients remaining constant. The composition had a burning time of 22.655 seconds/inch at 71° F. While this burning rate is within the range of the burning rates of U.S. Pat. No. 3,028,229, due to the amount of tungsten and chromate present, the burning rate is still slower than a corresponding composition without fluoride.

The effect of pressure on a system containing calcium fluoride as opposed to a system without calcium fluoride is shown as follows. The firing test performed on the composition of this example was repeated on an obturated system rather than upon a vented system. Whereas the vented system produced a burning rate of 22.655 seconds/inch, the obturated system with its increased pressure, produced a burning rate of 18.274 seconds/inch. Thus, the percent difference between the vented and obturated burn times is 19.34%. This is compared with a composi-

4

tion suggested by U.S. Pat. No. 3,028,229, i.e. 29.2 percent tungsten, 55.8 percent barium chromate, 10 percent potassium perchlorate and 5 percent diatomaceous earth. The vented burning rate at 71° F. for this system was 23.762 while the obturated burning rate was 15.061. Thus, the percent difference between the vented and obturated burn times is 36.62%, or almost twice as much as the percent difference with the fluoride (i.e. 19.34%). Thus, not only does the fluoride provide the unexpected result of slower burning time, but it also makes the composition less pressure dependent.

EXAMPLE IV

This example shows the effect of replacing 5 percent of diatomaceous earth with 5 percent of calcium fluoride on the burning rates of various compositions containing 10 percent potassium chlorate and a balance of barium chromate.

Percent tungsten	Burning rate with—	
	(a) CaF ₂	(b) SiO ₂
25	61.034	34.008
30	40.118	22.376
35	20.138	15.106
45	12.918	8.743
55	8.214	5.509

Thus, a much slower burning rate is achieved by replacing diatomaceous earth in the composition of U.S. Pat. No. 3,028,229, with calcium fluoride.

The pyrotechnic time delay compositions of the instant invention can be used wherever time delay compositions have heretofore been used, such as in cartridges, fuzes, ordnance devices requiring time delay, etc.

Obviously, numerous modifications and variations of the present invention are possible in 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 herein.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A pyrotechnic time delay composition comprising tungsten, potassium perchlorate, barium chromate and a low melting compound selected from the group consisting of calcium fluoride, strontium fluoride, ceric fluoride, magnesium fluoride, and mixtures thereof, wherein the amount of potassium perchlorate is less than the stoichiometric equivalent of the tungsten present in said composition.

2. The composition of claim 1 wherein the composition additionally contains diatomaceous earth.

3. A composition according to claim 2, which contains, on a weight percent basis; from about 10-90 percent of tungsten, from about 4.5 to about 15 percent of potassium perchlorate; from about 10 to about 60 percent barium chromate; from about 3 to about 12 percent of diatomaceous earth; and up to 5 percent of said low melting compound.

4. A composition according to claim 1 wherein said low melting compound is selected from the group consisting of calcium fluoride, strontium fluoride, magnesium fluoride and ceric fluoride.

5. A composition according to claim 1 wherein said low melting compound is calcium fluoride.

6. A composition according to claim 3 wherein said low melting compound is calcium fluoride.

7. A composition according to claim 6 wherein both the calcium fluoride and the diatomaceous earth are present in the amount of about 3 weight percent.

8. A composition according to claim 7, containing:

	Percent
Tungsten	32
Barium chromate	52
Potassium perchlorate	10
Diatomaceous earth	3
Calcium fluoride	3

5

9. A composition according to claim 7, containing:

	Percent
Tungsten -----	24
Barium chromate -----	60
Potassium perchlorate -----	10
Diatomaceous earth -----	3
Calcium fluoride -----	3

10. A composition according to claim 5, containing:

	Percent
Tungsten -----	25
Barium chromate -----	60
Potassium perchlorate -----	10
Calcium fluoride -----	5

6

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