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PYROTECHNIC COMPOSITIONS

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10 Claims. (Cl. 149—40)

This invention relates in general to certain new and useful improvements in pyrotechnic compositions and, more particularly, to pyrotechnic compositions having predetermined burning rates by reason of which such compositions can be utilized as so-called "delay mixtures."

Compressed columns of solid powder mixtures have long been used for initiating some desired pyrotechnic result under time delay 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. More recently, 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.

All existing types of so-called "delay mixtures," however, are subject to a number of serious limitations. Where the mixture must perform reliably extremes of low temperature within the range of −65° F. to −90° F. in a reasonsably narrow column not exceeding 0.250 inch in diameter, the range of burning time per lineal inch is restricted to a maximum of about 10–13 seconds. Many of the conventional delay mixtures not only fail to perform reliably extremes of temperature, but are also subject to undesirable variations in burning rate responsive to changes in temperature. Furthermore, such delay mixtures are extremely sensitive to pressure changes. Consequently, if substantial quantities of gas are evolved during burning, the internal pressure build-up will cause the delay mixture to burn erratically.

Most existing types of delay mixtures are not ignitible in a rarefield atmosphere or, at least, do not burn consistently under such conditions. In addition, the formulation of conventional delay mixtures has been such that the electrical conductivity of the mixture is low both before and after the pyrotechnic reaction. This matter of electrical conductivity is not, of course, particularly significant for delay trains as such but constitutes a serious deficiency where the delay train is utilized in multi-stage rockets and similar modern applications.

It is, therefore, one of the primary objects of the present invention to provide pyrotechnic compositions, or so-called delay mixtures, which react exothermically without producing any appreciable quantity of gaseous reaction products and, therefore, are not adversely affected by either internal or ambient pressure conditions.

It is another object of the present invention to provide pyrotechnic delay mixtures which have a very broad range of burning times and which will perform reliably over a wide range of ambient temperatures.

It is a further object of the present invention to provide pyrotechnic delay mixtures which are easily ignitible, consistently burning, chemically stable, precisely reproducible, and which produce very compactly sintered residues.

It is likewise an object of the present invention to provide pyrotechnic compositions of the type stated which are electrically conductive both before and after ignition.

Broadly speaking, the present invention resides in the

discovery that finely divided or powdered metals of the class consisting of chromium, molybdenum and wolfram can be intimately intermixed with potassium perchlorate and a secondary oxidizer, the quantity of potassium perchlorate being less than the stoichiometric equivalent of the metal powder present in the mixture. Such mixtures form a pyrotechnic composition which, when compressed into a column of selected cross-sectional area, will have a precisely predetermined lineal burning rate. Moreover, compositions formulated in accordance with the present invention have extremely low gas evolution and, therefore the burning rate is not rendered erratic due to pressure changes. Within the scope of the present invention, the primary oxidizer is finely powdered potassium perchlorate. The secondary oxidizer, which acts as a reaction modifier to slow the burning rate, is, preferably, barium chromate, but numerous other oxidizers which contain no potentially volatile components except oxygen have proven to be satisfactory, such as, for example, all metal chromates and all heavy metal oxides. More particularly, the following are substances which have been found to function effectively as secondary oxidizers: Barium chromate, strontium chromate, calcium chromate, silver oxide, barium peroxide, manganese dioxide, cupric oxide, and lead dioxide.

As heretofore noted, it is an essential part of the present invention that the pyrotechnic composition contain substantially less potassium perchlorate than stoichiometrically combines with the metal regardless of other ingredients which may be present. The other ingredients may consist of varying amounts of barium chromate and excess metal or excess metal alone without addition of barium chromate. These mixtures evolve only as much gas as is liberated due to incidental presence of gas formers such as adsorbed gases or unremovable traces of moisture.

It has been found in connection with the present invention that chromium or molybdenum containing mixtures are best suitable for extremely reliable combinations in the conventional burning rate ranges, namely, from 1 to 10 second per inch. Molybdenum also forms excellent mixtures below one second per inch of burning time. Tungsten containing mixtures form reliably burning mixtures of as high as 40 seconds per inch. For all tungsten containing mixtures which range from about 1 to 40 sec./in., it has been found that the addition of siliceous matter, such as finely ground calcined infusorial earth has a beneficial effect on the control of compaction and upon the reproducibility of the burning rate.

Example I

	Percent by wt.
Powdered metallic chromium	80
Finely divided potassium perchlorate	10
Finely divided barium chromate	10

Burning rate—1.5 sec./in.

Example II

Powdered metallic chromium	50
Finely divided potassium perchlorate	25
Finely divided barium chromate	25

Burning rate—7 sec./in.

Example III

Powdered metallic chromium	55
Finely divided potassium perchlorate	10
Finely divided barium chromate	10
Finely divided silver	25

Burning rate—1.5 sec./in.

Example IV

	Percent by wt.
Powdered metallic molybdenum	90
Finely divided potassium perchlorate	10
Finely divided potassium cerchlorate	10

Burning rate—0.1 sec./in.

Example V

Powdered metallic molybdenum	33.25
Finely divided potassium perchlorate	9.5
Finely divided barium chromate	52.25
Finely ground calcined infusorial earth (diatomaceous earth)	5.0

Burning rate—6 sec./in.

Example VI

Powdered metallic molybdenum	30
Finely divided potassium perchlorate	5
Finely divided barium chromate	65

Burning rate—18 sec./in.

Example VII

Powdered metallic tungsten	79.54
Finely divided potassium perchlorate	4.85
Finely divided barium chromate	12.61
Finely ground calcined infusorial earth (diatomaceous earth)	3

Burning rate—1.4 sec./in.

Example VIII

Powdered metallic tungsten	49.5
Finely divided potassium perchlorate	4.5
Finely divided barium chromate	36.0
Finely ground calcined infusorial earth (diatomaceous earth)	10

Burning rate—10 sec./in.

Example IX

Powdered metallic tungsten	38.00
Finely divided potassium perchlorate	4.75
Finely divided barium chromate	52.25
Finely ground calcined infusorial earth (diatomaceous earth)	5

Burning rate—20 sec./in.

Example X

Powdered metallic tungsten	30.8
Finely divided potassium perchlorate	8.8
Finely divided barium chromate	48.4
Finely ground calcined infusorial earth (diatomaceous earth)	12.0

Burning rate—30 sec./in.

Example XI

Powdered metallic tungsten	26.6
Finely divided potassium perchlorate	9.5
Finely divided barium chromate	58.9
Finely ground calcined infusorial earth (diatomaceous earth)	5

Burning rate—40 sec./in.

Because all these compositions are rich in metal fuel and contain a considerable amount of unreacted metal after burning, they are mostly good conductors for electricity before and after reaction. Such conductivity can be further enhanced by replacing some of the excess metal by an inert but electrically highly conductive metal, such as silver powder. By embedding metal wires insulated with a suitable thin organic coating into the delay column, it is possible to close electric currents triggered by the burning off of the insulation coating due to the advancing glow front and the establishing of electrical contact between the delay column and the wire and thus affect in an extremely simple manner an electric activation or a series of such activations at specified time intervals.

The foregoing functions are greatly aided by the fact that all the compositions of the present invention form extremely compact, sintered and highly cohesive residues which are fully retained within the delay column during and after burning. This property makes the delay mixtures suitable for activation during exertion of high spin rates, set-back forces, acceleration and deceleration, shock and vibration. A further advantage of the invention is that the metal powders employed are more or less "passive" to oxidation by aid and hardly affected by water, so that it is not necessary to treat them with protective coatings as has formerly been practiced with certain metal powders and which is a tedious and costly burden for the manufacturer. In addition, the metals of the present invention are not easily ignited by sparks or other accidental means. The mixing of the ingredients can be done safely in small quantities by dry mixing, such as repeated screening, but because of the potential hazard innate in all pyrotechnic loose powder mixtures, it is preferable to mix larger quantities by vigorous mechanical stirring in slurry form in an easily removable liquid, such as methanol. Furthermore, the pyrotechnic compositions of the present invention can be formulated by varying the proportions of the metal powders and oxidizers to achieve variations in burning times from a fraction of one second to forty seconds per lineal inch. It has also been found that the pyrotechnic compositions of the present invention perform reliably over wide variations in ambient temperature ranging from −165° F. to +165° F. The temperature coefficients of the pyrotechnic mixtures over the aforesaid ambient temperature range does not exceed a maximum of 0.08% per degree F. The gas evolution of the pyrotechnic mixtures of the present invention does not exceed 10 ml. of gas per gram of mixture at standard conditions of temperature and pressure, a factor which is far below previously experienced values and is of great advantage in fuse design.

It should be understood that changes in the methods, compositions, and combinations above set forth may be made without departing from the nature and principle of my invention.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:

1. A pyrotechnic composition having substantially the following constituency:

	Percent by weight
Powered metallic chromium	80
Finely divided potassium perchlorate	10
Finely divided barium chromate	10

2. A pyrotechnic composition having substantially the following constituency:

	Percent by weight
Powdered metallic chromium	50
Finely divided potassium perchlorate	25
Finely divided barium chromate	25

3. A pyrotechnic composition having substantially the following constituency:

	Percent by weight
Powdered metallic chromium	55
Finely divided potassium perchlorate	10
Finely divided barium chromate	10
Finely divided silver	25

4. A pyrotechnic composition having substantially the following constituency:

	Percent by weight
Powdered metallic molybdenum	33.25
Finely divided potassium perchlorate	9.5
Finely divided barium chromate	52.25
Finely ground calcined infusorial earth (diatomaceous earth)	5.0

5. A pyrotechnic composition having substantially the following constituency:

	Percent by weight
Powdered metallic molybdenum	30
Finely divided potassium perchlorate	5
Finely divided barium chromate	65

6. A pyrotechnic composition having substantially the following constituency:

	Percent by weight
Powdered metallic tungsten	79.54
Finely divided potassium perchlorate	4.85
Finely divided barium chromate	12.61
Finely ground calcined infusorial earth (diatomaceous earth)	3.

7. A pyrotechnic composition having substantially the following constituency:

	Percent by weight
Powdered metallic tungsten	49.5
Finely divided potassium perchlorate	4.5
Finely divided barium chromate	36.0
Finely ground calcined infusorial earth (diatomaceous earth)	10.

8. A pyrotechnic composition having substantially the following constituency:

	Percent by weight
Powdered metallic tungsten	38.00
Finely divided potassium perchlorate	4.75
Finely divided barium chromate	52.25
Finely ground calcined infusorial earth (diatomaceous earth)	5.

9. A pyrotechnic composition having substantially the following constituency:

	Percent by weight
Powdered metallic tungsten	30.8
Finely divided potassium perchlorate	8.8
Finely divided barium chromate	48.4
Finely ground calcined infusorial earth (diatomaceous earth)	12.0

10. A pyrotechnic composition having substantially the following constituency:

	Percent by weight
Powdered metallic tungsten	26.6
Finely divided potassium perchlorate	9.5
Finely divided barium chromate	58.9
Finely ground calcined infusorial earth (diatomaceous earth)	5.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Donald E. Olander

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 16, for "predettermined" read -- predetermined --; lines 29 and 35, after "reliably", each occurrence, insert -- at --; column 3, line 5, for "potassium cerchlorate" read -- barium chromate --.

Signed and sealed this 19th day of February 1963.

(SEAL)
Attest:

ESTON G. JOHNSON
Attesting Officer

DAVID L. LADD
Commissioner of Patents