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PERCUSSION SENSITIVE PYROTECHNIC OR PYROPHORIC ALLOY-TYPE PRIMING MIXTURE

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This invention relates to the production of percussion sensitive explosive compositions having particular utility as priming mixtures for ammunition.

A substantial number of pyrophoric alloys are known which may be identified generally as those alloys which on being struck or abraded will have fine particles released therefrom which will spontaneously ignite in brilliant sparks capable of igniting gases, alcohol, naphtha, and other inflammable substances. Such alloys find their widest use as "flints" for cigarette lighters, miners lamps, welders torches, etc. Probably the most widely used of such alloys include as their principle active ingredients metals of the rare earth family, such as cerium, lanthanum and others, frequently modified by the addition of iron, magnesium or other metals, to vary the nature of the sparks produced, hardness or other properties. One of the commonest of these rare earth alloys is known as "misch" metal, the exact composition varying somewhat with different manufacturers. Other known pyrophoric alloys contain one or both of the active metals titanium and zirconium alloyed in various combinations with lead, tin, aluminum, antimony, manganese, bismuth and silicon. A common characteristic of these alloys appears to be that when finely divided fresh clean surfaces are produced in air or in contact with other oxygen bearing media, the alloy ignites spontaneously. Some active metals appear to form protective oxide films so rapidly when a clean surface is exposed that no substantial reaction takes place and these are not considered to be pyrophoric metals. Aluminum is an outstanding example of this effect. For use in percussion priming mixtures, it is also necessary that the alloys have such characteristics of strength and brittleness as to fracture readily and produce clean reactive surfaces under the action of a firing pin below.

We have discovered that virtually any of the pyrophoric alloys which are sufficiently active to be used efficiently as lighter "flints" can be used in admixture with active oxidizers to produce sensitive priming mixtures which will react with explosive violence under the stimulus of percussion.

Since none of the essential constituents of such a mixture are of themselves explosive, it follows that such mixtures are safer to prepare and to handle in a primer manufacturing operation than are the conventional fulminating explosive heretofore used.

An added and unexpected advantage of such primer mixtures is their extraordinarily high degree of stability when exposed to elevated temperatures for extended periods of time.

For some applications it may be desirable to modify or to sensitize the mixtures by the employment of explosive ingredients such as 1-guanyl-4-nitrosoaminoguanyltetrazene commonly known as tetrazene or tetracene. But even when so modified, the mixtures are still far safer to handle than mixtures employing the conventional initiating explosives. Similarly auxiliary fuels, frictionators, and other primer modifying expedients may be resorted to in accordance with principles known in the explosives art.

The exact nature of the invention will become more apparent from consideration of the following specification in which there will be discussed in order (1) the suitable and preferred pyrophoric metals, (2) the suitable and preferred oxidizers, (3) suitable ingredients for modifying the sensitivity and other characteristics of the compositions and (4) an illustrative group of priming mixtures employing these ingredients.

PYROPHORIC ALLOYS

In general, a pyrophoric alloy has been defined as one which has the property of emitting sparks when scratched or struck with steel and such active pyrophoric alloys as misch metal are widely used as flints in lighters and other igniting devices for gases. Misch metal has been defined as a pyrophoric alloy which consists of a crude mixture of cerium, lanthanum, neodymium and other rare earth metals in the approximate ratio in which they occur in monazite sand and misch metal is usually obtained by electrolysis of a fused mixture of the chlorides of these metals. Although the specific composition of misch metal may vary somewhat with the producer, a typical composition is as follows:

	Percent
Cerium	50
Lanthanum	40
Other rare earth metals	3
Iron	7

Various producers of pyrophoric alloys modify misch metal of substantially the above composition by alloying it or mixing it with aluminum or magnesium. Thus, one producer has available compositions of 80% misch metal and respectively 20% magnesium and 20% aluminum.

The active metals titanium and zirconium, although not ordinarily regarded as pyrophoric because of the rapidity with which they form tenacious protective oxide coatings, form the base, when alloyed with other metals, of several other useful pyrophoric alloys.

The following table shows the composition of various pyrophoric alloys tested.

TABLE I.—PYROPHORIC ALLOYS

Zirconium	---	---	---	25	25	20	---	35	---	50	---	---	---	---
Titanium	45	45	50	25	25	20	---	---	8	---	35	---	---	---
Lead	45	45	---	---	50	60	---	35	---	20	---	---	---	---
Antimony	---	---	---	---	---	---	---	3	30	---	28	---	---	---
Manganese	---	---	---	---	---	---	---	27	62	---	2	---	---	---
Tin	10	---	---	50	---	---	---	---	---	30	---	---	---	---
Bismuth	---	---	---	---	---	---	---	---	---	---	35	---	---	---
Aluminum	---	---	---	---	---	---	---	---	---	---	---	20	---	---
Silicon	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Iron	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Cerium	---	10	50	---	---	---	---	---	---	---	---	---	---	---
Yttrium	---	---	---	---	---	---	80	---	---	---	---	---	---	---
Magnesium	---	---	---	---	---	---	20	---	---	---	---	20	---	---
Misch metal	---	---	---	---	---	---	---	---	---	---	---	80	80	75
Iron	---	---	---	---	---	---	---	---	---	---	---	---	---	25

With some modifications in specific primer composition, it is felt that the above or any other pyrophoric alloy exhibiting the characteristic of emitting showers of sparks when struck or abraded can be used.

In general, it is preferred to use the pyrophoric alloys in granulations of such size that all particles may be passed through a 250 mesh screen.

OXIDIZERS

Satisfactory performance of pyrophoric alloys in percussion primers requires that they be used in combination with active oxidizing agents. Barium nitrate ($Ba(NO_3)_2$) has been used as the main oxidizer in most of the experimental work, with lead dioxide (PbO_2) used as a more active supplemental oxidizer to improve the igniting efficiency of the mixtures. Other oxidizers which can be used for some purposes include potassium perchlorate ($KClO_4$) and red lead oxide (Pb_3O_4), potassium chlorate, ($KClO_3$) and lead nitrate ($Pb(NO_3)_2$). The latter two particularly are less desirable than barium nitrate and lead dioxide because of corrosive effects and because of

solubility in water, which tends to reduce the stability of the resulting primer mixture in long term storage under possible adverse moisture conditions.

ADDITION AGENTS AND TECHNIQUES FOR MODIFYING PRIMER MIXTURES

Although the essential elements of a pyrophoric primer as prepared in accordance with this invention are an active pyrophoric alloy and an active oxidizing agent in an intimate mechanical mixture, various modifications may be made to such a mixture to improve its storage stability, sensitivity, igniting power and other characteristics. Similarly, there are various handling techniques which may be employed in the production of the mixture which modify the characteristics of the mixture.

Among the measures which may be adopted to modify the igniting characteristics of the resulting priming mixtures are the addition to the mixture of various fuel supplements with appropriate adjustment of the oxidizer content of the mixture to maintain a satisfactory oxygen balance in the mixture. Suitable fuel supplements include finely divided powders of active metals such as magnesium, titanium and zirconium, hydrides of such metals, such as titanium and zirconium hydrides, and other fuel supplements, such as antimony sulfide, calciumsilicide, and sulfur. In addition to modifying the ignition characteristics of the mixtures, some of the materials mentioned above, such as zirconium and zirconium hydride, had the effect of increasing the sensitivity of the mixtures to percussion initiation probably because they are used in a fine powdered form which is so readily ignitible.

The effect of zirconium and zirconium hydride as sensitizers has been mentioned above. In addition, particularly where high sensitivity was required and high temperature stability was not a factor, it has been found that the addition of tetrazene, sometimes called tetracene (1-guanyl-4-nitrosoaminoguanyltetrazene) to the mixture has a desirable sensitizing action, as it has in other known priming mixtures.

Storage stability of these mixtures is in general satisfactory although the chemical activity of all of the ingredients must be considered. Those mixtures containing

only powdered pyrophoric alloys and inorganic oxidizers with no ingredients which are by themselves explosive are particularly stable when exposed for long periods at high temperatures (e.g., 6 hours at 500° F.).

The chemical activity of some of the active alloys considered has produced problems relative to stability under humid storage conditions or relative to use of such mixtures for wet charging or for dry charging with water or alcohol soluble binder solutions. These problems can usually be overcome by the use of binders which include neither alcohol or water, such binders being selected from those which are compatible with the active alloys and which are soluble in hydrocarbon solvents which are themselves compatible with the active alloys. For example, rubber cement dissolved in heptane appears to be a suitable binder. It has also been found that an alloy having substantially the proportions of 80% misch metal as hereinbefore defined and 20% magnesium can be stabilized by ball mill grinding, while submerged in heptane, for extended periods of time until the material is reduced to finer particle size than 325 mesh. This material appears to be stable even when employed in wet mixtures, stored under humid conditions or used with water-soluble binders or binders of shellac in alcohol. Polyacrylamide and/or silicone waterproofing agents in hydrocarbon solvents also function as compatible binders.

PRIMING COMPOSITIONS

Typical mixtures yielding reasonably satisfactory performance in powder ignition are tabulated below, with their sensitivity compared to standard products.

Table II relates primarily to the priming mixtures comprising the titanium-zirconium base pyrophoric alloys and Table III relates primarily to the priming mixtures comprising the misch metal based pyrophoric alloys.

In each of Tables II and III the sensitivity of the primers prepared with these mixtures is compared to the sensitivity of commercial lead styphnate priming mixtures loaded in the same type primer. The sensitivity values are tabulated as $\bar{X}$ in inch ounces which is the energy level at which 50% of the primers in a given sample lot fire in a conventional free drop test machine.

TABLE II.—PRIMING COMPOSITIONS, TITANIUM-ZIRCONIUM BASE ALLOYS

	PY-3	PY-12	PY-17	PY-21	PY-29	PY-109	PY-44	PY-124	PY-24	PY-116	PY-115	PY-152	PY-160	5061
Pyro Alloy:														
43 Ti, 47 Pb, 10 Sn	50	40	40	40	40	40			40					(1)
25 Ti, 25 Zr, 50 Sn							50	50				30		(1)
35 Zr, 35 Pb, 27 Mn, 3Sb										46			36	(1)
8 Zr, 62 Mn, 30 Sb											46			(1)
Potassium perchlorate									30					(1)
Barium nitrate	40	40	40	30	20	20	20	20		20	20	20	20	(1)
Lead dioxide				10	10	10	10	10	10	10	10	20	20	(1)
Zirconium (coarse)		20		20	20		20		20				10	(1)
Zirconium (−325 mesh)						16		16		20	20	7.5		(1)
Zirconium hydride			20											(1)
Magnesium	10													(1)
Antimony sulfide					10	10								(1)
Tetrazene						4		4		4	4	4	4	(1)
PETN												18.5	10	(1)
Sensitivity: [2]														
No. 72 Primer	80	32	36	40										16
No. 70 Primer				11	11	10	14	7	24	8	7	8	8	7

[1] Commercial lead styphnate mix. [2] $\bar{X}$ in inch ounces.

TABLE III.—PRIMING COMPOSITIONS, MISCH METAL ALLOYS

	PY-42	PY-43	PY-154	PY-55	PY-66	PY-76	PY-75	PY-95	5061
Pyro Alloy:									
75 misch metal and 25 Fe	50								(1)
80 misch metal and 20 Mg		50	50	46	36	36		21	(1)
80 misch metal and 20 Al							46		(1)
Potassium perchlorate			50						(1)
Barium nitrate	20	20		20	30	40	30	45	(1)
Lead peroxide	10	10		10	20	20	20	20	(1)
Zirconium (coarse)									(1)
Zirconium (−325 mesh)	20	20		20	10				(1)
Antimony sulfide								10	(1)
Tetrazene				4	4	4	4	4	(1)
Sensitivity, [2] No. 70 Primer	30	9	20	6	6	6	7	6	7

[1] Commercial lead styphnate mix. [2] $\bar{X}$ in inch ounces.

Many variations in mixtures may be made without departing from the teachings of this invention. Accordingly, the invention is not to be construed as limited to the specific examples above but only as defined by the claims appended hereto.

We claim:

1. A percussion sensitive ammunition priming mixture which comprises as its essential ingredients in an initimate mechanical mixture from about 25% to about 60% of an active pyrophoric alloy and from about 40% to about 70% of an active inorganic oxidizing agent selected from the group of active inorganic oxidizing agents consisting of barium nitrate, lead dioxide, potassium perchlorate, red lead oxide, potassium chlorate and lead nitrate.

2. A percussion sensitive ammunition priming composition which comprises an intimate mechanical mixture of a finely defined pyrophoric alloy and a finely divided active inorganic oxidizing agent selected from the group of active inorganic oxidizing agents consisting of barium nitrate, lead dioxide, potassium perchlorate, red lead oxide, potassium chlorate and lead nitrate, with a binder medium which is not chemically reactive with the pyrophoric alloy under any normal conditions of storage.

3. A percussion sensitive ammunition priming composition as defined in claim 1, including as an explosive sensitizer 1-guanyl-4-nitrosoaminoguanyltetrazene commonly known as tetrazene or tetracene.

4. A percussion sensitive ammunition priming composition as defined in claim 1 in which said oxidizing agent comprises a mixture of barium nitrate and lead dioxide.

5. A percussion sensitive ammunition priming composition as defined in claim 4 said barium nitrate being present in about twice the amount of lead dioxide included in the mixture.

6. A percussion sensitive ammunition priming composition as defined in claim 1 in which substantially 31% of a powdered pyrophoric alloy of misch metal and magnesium is in admixture with substantially 45% of powdered barium nitrate, substantially 20% of powdered lead dioxide, and substantially 4% of a sensitivity modifying agent.

7. A percussion sensitive ammunition priming composition as defined in claim 6 in which said composition includes as a binder medium a rubber cement utilizing heptane as a solvent.

8. A percussion sensitive ammunition priming composition as defined in claim 6 in which 1-guanyl-4-nitrosoaminoguanyltetrazene is used as a sensitivity modifying agent.

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