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[54] PYROTECHNIC COMPOSITION

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[57] **ABSTRACT**

The addition of transition metals or oxides or salts thereof, to pyrotechnic compositions containing conventional fuels and oxidizers, to greatly improve the luminous efficiency, average luminous output and propagative burning characteristics of such pyrotechnic compositions. The elements and compounds which are added also reduce the burning rate and lower the ignition temperature of such pyrotechnic compositions.

31 Claims, No Drawings

PYROTECHNIC COMPOSITION

This invention relates to improvements in pyrotechnic compositions by he incorporation of transition metals to increase the light emitting characteristics of such compositions so that they may be used advantageously in such things as military flares, delays, tracers and the like.

Pyrotechnic compositions, with few exceptions, are intimate mixtures of finely divided fuels and inorganic oxidants. The particle size of these components is normally in the micron range. Metals normally employed as fuels are aluminum and magnesium. Materials generally used as inorganic oxidants are nitrates, chlorates, and perchlorates of selected alkalis, alkaline earths and ammonium. Compositions used for pyrotechnics are usually made by blending metals and inorganic oxidants of the proper particle size, and by processing these ingredients to form an intimate mixture. For photoflash applications, the dry fuel-oxidant mixture is loaded directly into the item of interest. For flare applications, the fuel-oxidant mixture is further combined with (0–10 percent) of an organic binder and incrementally loaded into the flare device. The flares are then stored under carefully controlled conditions.

It is known that the burning rate of the above conventional pyrotechnic compositions can be varied to a limited extent by changing the particle size of the fuel. As the particle size of the fuel is increased, the burning rate is decreased. Decreasing the burning rate in this manner, however, is not advantageous because it generally results in a concomitant increase in erratic and flickering burning. Consequently, it is extremely difficult to make slow burning rate compositions which burn smoothly. It is further known that if a flare composition does not burn propagatively; i.e., in a continuous fashion, the composition can be made propagative by decreasing the particle size of the fuel, resulting in an increase in burning rate, or by adding organic promoters to the basic composition. Neither of these methods to achieve smooth burning cause an increase in luminous efficiency. The latter is a disadvantage if such compositions are to be used in military flares and the like.

As described above, most known methods of increasing luminous efficiency and achieving propagative burning are opposed to each other. Further, most known means of reducing the burning rate result in a decrease in the average luminous output. Prior to this invention, the usual method of increasing light intensity was to increase the size of the light emitting device, this, however, led to a decrease in its luminous efficiency. In pressed flare compositions, which has been incrementally loaded, erratic burning at the junctions between increments sometimes prevented propagative burning, with the result that the flares did not burn fully. In addition, higher temperatures were necessary in most cases to initiate burning.

The subject invention, the addition of the transition metals, salts and oxides, to the pyrotechnic compositions overcomes all the disadvantages of the prior art heretofore described. This is accomplished with the advantage that such pyrotechnic compositions are rendered capable of giving a greater luminous output with a slower burning rate resulting in a luminous efficiency heretofore not attainable. This advance in the art, herein described, is quite unexpected and forms, in effect, the basis of a discovery. In fact, the art teaches that certain transition metals may be added to combustible components to give the opposite results. For instance, the prior art teaches that the addition of such salts decreases the visible combustion zone thereby generally decreasing the light emitting characteristics.

An object of this invention is to provide an improved pyrotechnic composition which has significantly increased light emitting characteristics.

A further object of this invention is to provide an improved pyrotechnic composition which has greatly enhanced propagative burning characteristics.

Another object of this invention is to furnish a simple, improved, pyrotechnic composition which has a slow burning rate without having an accompanying decrease in light emitting characteristics.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same become better understood by reference to the following detailed description:

The present invention is the incorporation of either transition metals, salts or oxides thereof, into pyrotechnic composition having conventional fuels and oxidizers to impart greatly improved light emitting characteristics to said pyrotechnic compositions.

One of the effects of this invention is to provide a significant increase in the illumination available from pyrotechnic compositions. It also provides a simple, economical method of making flare and photoflash compositions which are more efficient and thereby more desirable in the many practical applications for which they can be used. More illumination is available from a given amount of reactants because of increased efficiency. Less unburned residue remains after burning. Less of the reactants are emitted as sparks thereby increasing safety. There is less of a chance that the flare will burn out too early as the propagative characteristics imparted by this invention are much greater than flares used without this invention. The temperature necessary to ignite the improved pyrotechnic composition comprised by this invention is less than that required for other pyrotechnic compositions not using this invention.

The selected transition metals which may be utilized to advantage in the present invention include Ti, V, Nb, Ta, Mo, W, Mn, and Zr.

Further, salts of the above metals, hydrated or anhydrous complex or simple may also be utilized to advantage. These include salts such as Na_2CrO_4, $VOSO_4$, $Zr(NO_3)_4 \cdot 5H_2O$ $Na_2WO_4 \cdot 2H_2O$, $KMnO_4$, $Na_2Cr_2O_7 \cdot 2H_2O$ and other alkali, alkaline earth and ammonium; chromates, dichromates and permanganates. Also, oxides of transition metals may be used within the concept of the present invention. Such oxides are Cr_2O_3, TiO_2, Fe_2O_3, MnO_2, Mn_3O_4, Mn_2O_3, ZrO_2, WO_3, MoO_3 and CrO_3.

The pyrotechnic compositions of the art which may be improved by the present invention are generally conventional and contain fuels an oxidizers, preferably containing a metallic fuel, such as Al, or Mg or mixtures or alloys of these metals, and containing an inorganic oxidizing agent, such as the alkali or alkaline earth nitrates, chlorates and perchlorates or ammonium nitrate, chlorate or perchlorate.

The following are examples of the general method of preparation of some representative pyrotechnic compositions into which this invention was incorporated:

EXAMPLE I

Enough sodium nitrate was ground in a rough surfaces mortar and pestle to perform the experiment. The ground sodium nitrate was then passed through a screen that would allow particles only 74 microns or less to pass through. 2.0g of the ground, screened, sodium nitrate was then introduced into a smooth surfaced mortar and pestle. 2.0g of atomized aluminum powder having an average particle size of 6 microns was then added to the prepared sodium nitrate in the smooth surfaced mortar and pestle. The two components were then mixed until an intimate blend was obtained. This intimate mixture represents a conventional loose pyrotechnic composition. To this intimate mixture was added powdered Mn_3O_4, Manganese (II, III) oxide to make 1.5 percent by weight and the whole was again blended in the smooth surfaced mortar and pestle until again an intimate mixture was obtained. This mixture is the improved, pyrotechnic composition of this invention.

A nonluminous igniter composition, to ignite the pyrotechnic compositions, was prepared by intimate mixing of finely divided tungsten, barium chromate and potassium perchlorate in such amounts that the final igniter composition contained 65 percent by weight tungsten, 25 percent by weight barium chromate and 10 percent by weight potassium perchlorate.

One hundred milligrams of the nonluminous igniter composition was tapped into a metal die, the die is simply a smooth hole 0.24 inches in diameter drilled through a stainless steel block. 300 milligrams of the improved pyrotechnic composition containing Mn_3O_4, previously described, was then introduced into the die, a metal punch made to fit the hole in the block was placed in the hole on top of the improved pyrotechnic composition and, the composition was pressed with a hydraulic laboratory press at approximately 30,000 psi for 30 seconds at ambient laboratory conditions (i.e. between 60°–85F and 20–70% relative humidity) to form a cylindrical grain 0.24 inches in diameter and 0.25 inches long. The nonluminous igniter composition and the improved pyrotechnic composition were processed in this manner because some mixing at the igniter pyrotechnic interface is necessary for proper initiation.

The previously described grain was then introduced into a laboratory chamber which was approximately 2 feed in diameter and 5 feet long, with a removable end, and with an aperture at the other end for measurements; subsequently, ignited with a hot wire in the chamber, and the resulting light output was measured with an RCA–926 vacuum phototube having Kodak No. 8(K2) corrective filters, yielding response characteristics essentially equivalent to those of the human eye. The voltage developed by the phototube current flowing through a standard resistor, (a helical, wire wound, 10 turn, variable resistor with a linear response), was recorded with a fast response, Honeywell Visicorder Oscillograph (Model No. 906C). The total light output of the phototube measured in volt-seconds, the duration of burning measured in seconds, the burning rate calculated as grams per second, the average luminous output calculated as volt-seconds per second, and the luminous efficiency calculated as volt-seconds per gram were determined and are reported in Table II.

A control grain was formulated in exactly the same manner set forth above except that the improvement of this invention, the transition metal oxide was not added. The grain was capped with the same igniter composition in the same manner and ignited in the previously described chamber. The illumination provided by the control grain was measured in the same manner as the illumination provided by the test composition and is reported in Table II as a control.

TABLE I

A number of experiments were performed in exactly the same manner as described in Example 1 except that different transition metals, and transition metal containing salts, and oxides were used and, in one case, the improvement of this invention was incorporated in the previously described manner into the standard pyrotechnic composition. The additives used to improve the composition are listed as follows:

Example	Additive	Amount—Percent by Weight
2	Mn_3O_4	5%
3	Cr_2O_3	2.5%
4	Cr_2O_3	6%
5	WO_3	7%
6	$Na_2Cr_2O_7 \cdot 2H_2O$	5%
7	TiO_2	5%
8	Fe_2O_3	5%
9	$VOSO_4$	5%
10	$Zr(NO_3)_4 \cdot 5H_2O$	7%
11	MoO_3	5%
12	Ti (finely divided)	5%
13	W (finely divided)	5%
14	Mo (finely divided)	5%
15	Mn (finely divided)	5%

Results of experiments performed with the additives listed in Table I were obtained in exactly the same manner and with exactly the same instruments used in Example 1, and these results are reported in Table II along with the results obtained in Example 1.

TABLE II

Example	Percent by weight additive to 1:1 weight ratio of Al/$NaNO_3$	Burning rate mean value	Percent decrease	Luminous output mean value	Percent increase	Luminous efficiency mean value	Percent increase
1	1.5% Mn_3O_4	0.2045	17	0.06637	5	0.3222	26
2	5% Mn_3O_4	0.1858	25	0.1329	111	0.7218	181
3	2.5% Cr_2O_3	0.2029	18	0.1128	79	0.5552	116
4	6% Cr_2O_3	0.1054	57	0.1329	111	1.253	388
5	7% WO_3	0.1740	29	0.8920	41	0.5115	99
6	5% $Na_2Cr_2O_7 \cdot 2H_2O$	0.1465	40	0.1369	117	0.9391	266
7	5% TiO_2	0.0822	67	0.06785	8	0.8271	222
8	5% Fe_2O_3	0.1225	50	0.1142	81.0	0.9182	258
9	5% $VOSO_4$	0.1096	55	0.1028	63	0.9426	267
10	7% $Zr(NO_3)_4 \cdot 5H_2O$	0.0979	60	0.04914	−22	0.5027	96
11	5% MoO_3	0.1622	34	0.08534	35	0.5263	105
12	5% Tis	0.1833	26	0.07753	23	0.4280	66
13	5% W	0.1839	25	0.1421	125	0.7765	203
14	5% Mo	0.2358	4	0.1528	142	0.6501	153
15	5% Mn	0.3963	+25	0.09555	51	0.3160	23
Control	No additives	0.2460		0.06309		0.2566	

It is evident from the results set forth in Table II that the improvements covered by the broad scope of this invention when incorporated into pyrotechnic compositions are extremely effective in increasing the visible radiation of said pyrotechnic compositions. Finely divided, selected transition metals such as Ti, W, Mo, increase the luminous efficiency by 23 to 200 percent. Powdered selected transition metal salts such as $Zr(NO_3)_4 \cdot {}^{085}H_2O$ and $VOSO_4$ provide an increase in the luminous efficiency of 96 to 267 percent. Powdered selected transition metal oxides, such as Cr_2O_3, TiO_2, Fe_2O_3 and selected transition metal salts such as $Na_2Cr_2O_7 \cdot 2H_2O$, $KMnO_4$ and other alkali, alkaline earth and ammonium dichromates and permanganates which can be used as a partial replacement for the inorganic oxidizer in the pyrotechnic composition, increase the luminous efficiency by 105 to 388 percent.

As taught by the prior art, there must be significant amounts of both fuel and oxidizer in the basic pyrotechnic composition, generally, in order to achieve propagative burning and produce an efficient device, from about 20 to about 80 weight percent fuel and from about 80 to about 20 weight percent inorganic oxidizer. Preferably, for the purposes of this invention, and to insure propagative burning and increased efficiency, the fuel can be present from about 30 to about 70 weight percent, and the inorganic oxidizer present from about 70 to about 30 weight percent. The best composition, for incorporation of our invention is from about 40 to about 60 weight percent fuel and from about 60 to about 40 weight percent inorganic oxidizer. The particle size of the fuel used, in order to achieve propagative burning and satisfactory efficiency can be from about 0.1 microns to about 50 microns, preferably to obtain better propagative burning and more efficiency, the particle size of the fuel can be between about 0.1 microns and about 30 microns. The best particle size for compositions into which our invention is incorporated, is between about 0.1 microns and about 20 microns. The particle size of the inorganic oxidizer is usually less than 100 microns in order to achieve a homogeneous mixture preferably the inorganic oxidizer particle size is less than 75 microns to insure that a homogeneous blend is obtained. Indeed as long as the inorganic oxidizer is powdered, it can be used in conjunction with the fuel to form a basic composition with which our improve-

ment can be incorporated to produce a large increase in the light emitting and propagative characteristics.

In the embodiment of this invention; selected, finely divided transition metals such as W, Mo and Ti, selected powdered transition metal oxides such as Cr_2O_3, MoO_3 and Fe_2O_3 and selected transition metal salts such as $VOSO_4$, $Na_2Cr_2O_7 \cdot 2H_2O$, $KMnO_4$ and $Zr(NO_3)_4.5H_2O$ can be used effectively from about 4 to about 12 weight percent in order to impart the greatly increased efficiency of our invention. If weight percentages outside these ranges are used, the efficiency of the improved composition is decreased. A preferred embodiment of this invention contains from about 4 to about 9 percent by weight of such finely divided transition metals and powdered salts and oxides of these transition metals efficiency is decreased outside these ranges. The optimum embodiment of this invention contains from about 5 to about 7 weight percent of such transition metals and transition metal compounds within this range the efficiency is greatly enhanced. In certain cases, selected transition metal salts such as $Na_2Cr_2O_7 \cdot 2H_2O$, $KMnO_4$ and other alkali, alkaline earth and ammonium chromates and dichromates, can be used to replace a portion of the inorganic oxidizer of the conventional pyrotechnic composition. In such cases the additive of our invention can be used in amounts higher than 12 weight percent. Indeed in some cases, the additive may be used effectively as long as the mixture burns propagatively.

From a referral to the prior art as compared to this present improvement in pyrotechnic compositions, it is obvious that an entirely unexpected result has been achieved. The utility of any pyrotechnic composition has been magnified by the simple expedient of incorporating selected transition metals, and salts and oxides containing selected transition metals into such pyrotechnic composition. The resulting increase in visible radiation is highly desirable especially in military flare and photoflash devices as it is possible to achieve a 388 percent increase in luminous efficiency by adding a minimal amount of the improvements of our invention and thereby only minimally increasing the size and weight of the item. No prior technique existed for this, increasing the luminous efficiency of pyrotechnic compositions.

It is evident that other selected transition metals and salts and oxides containing selected transition metals can be used in place of the specific compounds mentioned to achieve the same effect when incorporated into pyrotechnic compositions.

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.

We claim:

1. In a pyrotechnic illuminant composition comprising a finely divided metallic fuel selected from the group consisting of aluminum, magnesium, alloys consisting essentially of aluminum and magnesium, and mixtures thereof and an inorganic oxidizer selected from the group consisting of alkali nitrates, alkali chlorates, alkali perchlorates, alkaline earth nitrates, alkaline earth chlorates, alkaline earth perchlorates, ammonium nitrate, ammonium chlorate and ammonium perchlorate, said fuel and oxidizer present in a major amount, the improvement consisting of the incorporation of a minor amount of a transition metal selected from the group consisting of V, Nb, Ta, Mo, W and Mn, transition metal salts and transition metal oxides into said composition to impart greater light emitting characteristics.

2. The pyrotechnic composition of claim 1 wherein said salts are selected from the group consisting of Na_2CrO_4, $VOSO_4$, $Zr(NO_3)_4 \cdot 5H_2O$, $Na_2WO_4 \cdot 2H_2O$, $KMnO_4$ and $Na_2Cr_2O.2H_2O$.

3. The pyrotechnic composition of claim 1 wherein said oxides are selected from the group consisting of Cr_2O_3, TiO_2, Fe_2O_3, MnO_2, Mn_3O_4, Mn_2O_3, ZrO_2, WO_3, MoO_3 and CrO_3.

4. The pyrotechnic composition of claim 1 wherein said transition metals are present in an amount between about 4 and about 12 percent by weight of said pyrotechnic composition.

5. The pyrotechnic composition of claim 1 wherein said transition metals are present in an amount between about 5 and about 7 percent by weight of said pyrotechnic composition.

6. The pyrotechnic composition of claim 5 wherein said transition metal is V.

7. The pyrotechnic composition of claim 5 wherein said transition metal is Nb.

8. The pyrotechnic composition of claim 5 wherein said transition metal is Ta.

9. The pyrotechnic composition of claim 5 wherein said transition metal is Mo.

10. The pyrotechnic composition of claim 5 wherein said transition metal is W.

11. The pyrotechnic composition of claim 5 wherein said transition metal is Mn.

12. The pyrotechnic composition of claim 2 wherein said salts are present in an amount between about 4 and about 12 percent by weight of said pyrotechnic composition.

13. The pyrotechnic composition of claim 2 wherein said salts are present in an amount between about 5 and about 7 percent by weight of said pyrotechnic composition.

14. The pyrotechnic composition of claim 13 wherein said salt of a transition metal is Na_2CrO_4.

15. The pyrotechnic composition of claim 13 wherein said salt of a transition metal is $VOSO_4$.

16. The pyrotechnic composition of claim 13 wherein said salt of a transition metal is $Zr(NO_3)_4 \cdot b5H_2O$.

17. The pyrotechnic composition of claim 13 wherein said salt of a transition metal is $Na_2WO_4.2H_2O$.

18. The pyrotechnic composition of claim 13 wherein said salt of a transition metal is $KMnO_4$.

19. The pyrotechnic composition of claim 13 wherein said salt of a transition metal is $Na_2Cr_2O_7.2H_2O$.

20. The pyrotechnic composition of claim 3 wherein said oxides are present in an amount between about 4 and about 12 percent by weight of said pyrotechnic composition.

21. The pyrotechnic composition of claim 3 wherein said oxides are present in an amount between about 5 and about 7 percent by weight of said pyrotechnic composition.

22. The pyrotechnic composition of claim 21 wherein said oxide of a transition metal is Cr_2O_3.

23. The pyrotechnic composition of claim 21 wherein said oxide of a transition metal is TiO_2.

24. The pyrotechnic composition of claim 21 wherein said oxide of a transition metal is Fe_2O_3.

25. The pyrotechnic composition of claim 21 wherein said oxide of a transition metal is MnO_2.

26. The pyrotechnic composition of claim 21 wherein said oxide of a transition metal is Mn_3O_4.

27. The pyrotechnic composition of claim 21 wherein said oxide of a transition metal is Mn_2O_3.

28. The pyrotechnic composition of claim 21 wherein said oxide of a transition metal is ZrO_2.

29. The pyrotechnic composition of claim 21 wherein said oxide of a transition metal is WO_3.

30. The pyrotechnic composition of claim 21 wherein said oxide of a transition metal is MoO_3.

31. The pyrotechnic composition of claim 21 wherein said oxide of a transition metal is CrO_3.

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