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GREEN FLARE COMPOSITION

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ABSTRACT OF THE DISCLOSURE

The combination of a finely divided non-halogenated organic fuel such as an acetal resin and a chlorinated barium compound as an oxidizing material to produce a pyrotechnic composition emitting radiation in the green spectral region with minimal overtones of extraneous colors, thus enabling a positive color identification.

The invention described herein may be manufactured, used and licensed by or for the Government for governmental purposes without the payment to us of any royalty thereon.

BACKGROUND OF THE INVENTION

The present invention deals with a new and improved pyrotechnic composition and the use of this composition in flare candles and signals which on burning emit green colored flames.

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.

In the past, pyrotechnic flares and candles have been produced in a number of different colors for signalling purposes. However, the production of a satisfactory green flare has never been accomplished.

Military flare candles and signals which produce a green flame generally contain the following major ingredients: magnesium powder as the major fuel; barium nitrate as the oxidizer and color producer; hexachlorobenzene or polyvinyl chloride, both of which are chlorine donors as a color intensifier and copper dust which has also been used as a color intensifier; potassium perchlorate as an additional chlorine and oxygen source and as a burning rate regulator, and binder materials such as linseed oil and dextrin.

Flare candles and signals containing the above listed ingredients have been used for years in military items. The degree of green color saturation of the flames produced on burning these items has never been satisfactory for tactical applications, based upon the fact that the green color was polluted with white and red overtones, and in general appeared whitish-green to the eye. At longer viewing distances the red overtones generally predominated, leading to uncertainty as to the true color of the signal.

Theoretical and experimental studies have indicated that green color saturation is adversely affected by a number of variables such as temperature gradients in the flame, a high level background continuum due to magnesium oxide and light emission in the red spectral region. In order to minimize these deleterious effects, a study of newly available organic fuels as substitutes for the currently used magnesium was undertaken, based primarily on the lower flame temperatures that would be achieved through their use. The lower flame temperatures would reduce the extent of temperature gradient in the flame and reduce emission in the red spectral region based on grey body radiation. In addition, removing the magnesium would obviate the effect of background continuum due to

the magnesium oxide formed in the combustion process.

The subject invention, the use of powdered non-halogenated organic fuels together with a powdered chlorinated barium compound as oxidizing agent answers the needs of the art as described above, with special emphasis on the production of a pyrotechnic with a high percentage of light emission in the green spectral region. In addition, this invention eliminates the need for separate chlorine containing flame intensifiers.

It is therefore an object of this invention to provide a flare composition with a low flame temperature to reduce temperature gradient effects on light emission characteristics.

Another object is to provide a green flare with reduced light emission in the red spectral region based on grey body radiation.

Yet another object is to provide a green flare with a reduced background continuum by substantially eliminating mangesium combustion.

A further object is to provide an easily identifiable substantially monochromatic green flare which does not change color when attenuated by atmospheric conditions.

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 description:

This discovery, herein described forms the basis for an advance in the art. The production of an easily identifiable green flare composition provides a broader spectrum of flares for use in numerous situations. In addition the use of this novel flare composition enables identification in atmospheric conditions and at distances which previously prevented the satisfactory use of green as a flare signal color.

The following range of composition may be used to prepare the pyrotechnic compositions of our invention

	Parts by weight
Comminuted, non-halogenated, solid organic fuel	20–30
Finely divided metallic fuel	0–15
Chlorinated, inorganic barium oxidizer	60–80
Additives	0–5
Binder	0–5

The powdered solid organic fuels which may be used to advantage with our invention are any organic substances which produce a substantial proportion of green light when burned in the composition of our invention. Preferably, fuels such as asphaltum and acetal resins such as Delrin (a trademarked acetal resin of E. I. du Pont de Nemours & Co.) may be employed. Delrin is a thermoplastic polymer of formaldehyde in a highly crystalline stable form characterized by repeating oxymethylene units $[—OCH_2—]_n$ in the polymeric structure. Other acetal resins may be used as organic fuels in the composition of our invention such as Celcon (a trademark of Celanese Corp. of America).

The inorganic fuels which may be used are any finely divided metallic fuels which produce substantial amounts of green light when burned with the composition of our invention. Preferably, in order to increase the candlepower level and burning rate of this composition a preselected amount of magnesium powder may be substituted for a like weight of the inorganic barium oxidizer. The amount of metallic fuel is determined by the candlepower desired in conjunction with production of the desired percentage of green light and the most favorable burning rate for use with the flare.

It is theorized that the radical $BaCl^+$ (barium sub chloride) is the prime species in a flame producing green light and therefore any barium compound which will produce this species can be used without additional chlorine donor flame intensifiers. Preferably barium chlorate and

perchlorate including the hydrated and anhydrous forms are used to produce a large amount of green light. In addition to production of green light vigorous oxidation is necessary. Therefore the choice of oxidizer must be governed by criteria of both green light production and oxidation capacity.

Silicon or boron powder may be added to increase the light output without substantially detracting from the green light.

The binders that may be used are any common binders used in flare compositions which do not substantially detract from the amount of green light. Preferably the binders used are solutions of vinyl alcohol acetate or solutions of Viton A (a trademark of E. I. du Pont de Nemours & Co.). Viton A is a copolymer of hexafluoropropylene and vinylidene fluoride.

Generally, the particle size of the components of our invention is governed by parameters of burning rate in the composition and flame propagation through the composition. If the particle size is too small the burning rate will be to rapid. If the particle size is too large propagation will not take place.

For the solid organic fuels a particle size of about 20 to about 60 microns is preferred. For the oxidizer a particle size of about 1 to about 30 microns is preferred. The silicon powder particle size preferred is about 1 to about 40 microns. The boron powder used is commercial grade powder which is usually one micron or less in size.

The composition of this invention, which may be used to produce a pryotechnic composition having the properties desired, is set forth in the following examples. It is, of course, understood that these examples are meant to be illustrative and not restrictive of our invention.

EXAMPLE 1

37.5 grams of Delrin acetal resin of about 40 micron particle size and 112.5 grams of powdered barium chlorate monohydrate of about 14 micron particle size, as measured by the air permeability method, were blended to form a pyrotechnic composition. Prior to blending the barium chlorate ($Ba(ClO_4)_2 \cdot H_2O$) was oven dried at 105° C. for one hour to remove surface moisture. The required percentage weight of each ingredient was dry blended in an atmosphere of low humidity at ambient temperatures and pressures and placed in a rubber container together with an equal weight of small rubber stoppers, the latter being added to improve the uniformity of the final blend. The rubber container was sealed by taping the cover, and the container and contents were rotated by remote control for a period of thirty minutes, after which the entire contents were transferred to a No. 16 mesh sieve for the purpose of separating the rubber stoppers from the powdered mixture. Thereafter the powdered mixture is loaded into flare or signal cases at a loading pressure of about 7,000 pounds per square inch and ignited with a conventional flare igniter composition. The percentage of light falling into specific color regions was determined using a flare radiometer. The radiometer is designed to record the visible spectrum of a varying flame source, thus making it possible to determine the relative amounts of each color in the total light output of a flare or signal.

A number of compositions were formulated in exactly the same manner as described in Example 1 and are listed in Table 1. The components of the compositions were varied, and then tested. Also a standard flare composition was formulated and tested using the above described method.

TABLE 1.—COMPARATIVE COMPOSITIONS

[Percent by weight]

Formulation	Standard	A	B	C	D	E	F	G	H	I	J	K	L
Delrin powder, 56 micron		25	12.5	25	15	35	50			23.7	23.7	25	25
Barium chlorate, 14 micron, monohydrate		70	37.5	60	85	65	50	75	75	71.3	71.3	72	72
Atomized magnesium powder, 200/325 mesh		5	50	15									
Magnesium, granulation 11,[1] coated with linseed oil	16												
Potassium perchlorate	12												
Barium nitrate	51												
Copper dust	1												
Hexachlorobenzene	12												
Linseed oil	3												
Dextrin powder	5												
Polyvinyl chloride									25				
Chlorinated polyethylene								25					
JAN-S-230 silicon powder, 20 micron										5			
Boron powder, 1 micron											5		
Viton A resin (in solution)												3	
Vinyl alcohol acetate resin (in solution)													3

[1] Granulation 11 magnesium is equivalent to 80/200 mesh.

Results of experiments performed with the compositions listed in Table 1 were obtained by conventional methods. These results are reported in Table 2 along with the results obtained from Example 1.

TABLE 2.—COMPARATIVE RESULTS

Formulation	Standard	A	B	C	D	E	F	G	H	I	J	K	L	Example
Candlepower, kilocandles	4.7	0.74	62.3	2.2	0.23	[1]	[1]	0.3	0.4	0.2	0.3	0.2	0.1	.35
Burning rate, in./min	2.7	2.8	7.7	3.6	2.9			2.1	3.2	3.0	4.1	2.4	1.9	2.6
Radiometric data:														
Violet, percent	2.9	0	2.9	0	2.2			2.4	3.3	1.6	1.2	2.2	0	0
Blue, percent	13.7	12.3	15.9	15.6	11.6			6.2	8.3	8.6	10.7	12.1	10.3	9.7
Green, percent	35.9	60.0	34.0	51.5	41.4			16.8	18.4	54.0	52.2	46.9	54.5	61.9
Yellow, percent	5.0	6.7	6.8	6.8	7.9			7.3	7.4	8.7	10.1	7.6	6.3	9.8
Orange, percent	5.2	3.9	5.9	5.6	7.2			9.9	8.5	6.4	5.7	4.0	4.9	5.2
Red, percent	37.3	17.1	34.5	20.5	29.7			57.4	54.1	20.7	20.1	27.2	24.0	13.4

[1] Burned erratically, no measurable light output.

It is evident from the results set forth in Table 2 that the compositions covered by the broad scope of this invention are extremely effective in producing a substantial percentage of green light out of the total spectrum of the flare composition.

It can be seen that there is an increase from 35.9 percent green light in a standard flare to 61.9 percent in the composition of Example 1, which contained 25 percent Delrin and 75 percent barium chlorate monohydrate. Formulations D, E and F show the result of changing the amount of Delrin with a concomitant adjustment in the

amount of barium chlorate monohydrate. At 15 percent Delrin there was an increase from the standard 35.9 to 41.4 percent in the green light output but this was not as great as in Example 1. At percentages of 35 and above the flares burned too erratically to measure their light output. Formulations I and J show the effect of the silicon and boron additives. The burning rate is increased substantially and there is a small decrease in the percentage of green light produced as compared to Example 1, yet it is still much higher than the standard. Examples K and L show the effect of binders on the system and it is evident that although there was some decrease from Example 1 the percentage of green light is still substantially higher than the standard formulation. Examples A, B and C show the effect of adding magnesium to the composition to increase the candlepower. At the 5% level as shown in formulation A the candlepower is more than doubled, the burning rate remains approximately equivalent and the percentage of green light remains about the same. In B and C the amount of magnesium used was increased and it can be seen that above a certain point the use of magnesium becomes disadvantageous. Formulations G and H show the effect of using certain halogenated organic fuels. The percentage of green light was much less than that produced by Example 1.

From a referral to the prior art as compared to the present invention it is obvious that a much higher percentage of green light has been obtained by the use of our invention. The utility of green flares for use in adverse atmospheric conditions and at great distances has been enhanced and indeed the use of green flares as a signal that can be reliably identified has been permitted.

It is evident that other selected comminuted non-halogenated organic fuels and inorganic barium oxidizers containing chlorine can be used in place of the specific compounds mentioned to achieve the same effect when used to formulate pyrotechnic compositions.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. We, therefore, wish it to be understood that we do not desire to be limited to the exact details described.

We claim:

1. A pyrotechnic composition adapted for use in a flare producing green light consisting essentially of an intimate mixture of a finely divided nonhalogenated organic fuel and a finely divided inorganic oxidizing compound containing barium and chlorine, said inorganic oxidizing compound being present in an amount greater than said fuel.

2. A pyrotechnic composition as defined in claim **1** wherein said fuel is an acetal resin.

3. A pyrotechnic composition as defined in claim **1** wherein said fuel is asphaltum.

4. A pyrotechnic composition as defined in claim **1** wherein the particle size of said fuel is from about 20 to about 60 microns and the particle size of said oxidizer is from about 1 to about 30 microns.

5. A pyrotechnic composition as defined in claim **1** wherein said inorganic oxidizer is selected from the group consisting of anhydrous barium chlorate, hydrated barium chlorate, anhydrous barium perchlorate, hydrated barium perchlorate and mixtures thereof.

6. A pyrotechnic composition as defined in claim **1** consisting essentially of:

	Parts by weight
Acetal resin fuel	20–30
Finely divided metallic fuel	0–15
Inorganic oxidizing compound containing barium and chlorine	60–80
Additives	0–5
Binder	0–5

7. A pyrotechnic composition as defined in claim **6** wherein said additives are present in an amount up to about 5 parts by weight of said composition, said additives being selected from the group consisting of silicon powder and boron powder.

8. A pyrotechnic composition as defined in claim **6** wherein said finely divided metallic fuel is magnesium present in an amount up to about 15 parts by weight of said composition.

9. A pyrotechnic composition as defined in claim **6** wherein said binder is present in an amount up to about 5 parts by weight of said composition said binder being selected from the group consisting of vinyl alcohol acetate and a copolymer of hexafluoropropylene and vinylidene fluoride.

10. A pyrotechnic composition as defined in claim **6** consisting of 25% by weight acetal resin and wherein said inorganic oxidizer is barium chlorate monohydrate present in the amount of 75% by weight of the composition.

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