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The Effect of Hot Spots on Burning Surface and Its Application to Strobe Light Formation with Mixtures Which Contain No Ammonium Perchlorate

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ABSTRACT

The objective of this work was to make clear the effect of hot spots or hot spot materials on burning pyrotechnic compositions and to find practicable strobe light compositions without ammonium perchlorate which is not always popular in the firework field, using the effect of hot spot materials.

As the hot spot materials, four types, Japanese oak charcoal, red iron, red lead, and potassium dichromate were selected from many substances. The effect of each was examined by burning tests of compositions which contained rosin, usual oxidizers (ammonium perchlorate, potassium perchlorate, and potassium nitrate), and a small quantity of each hot spot material. In this case, the effects did not clearly appear except that of potassium dichromate, which promoted the burning rate of compositions in fairly large extent.

Secondly, the effect of red lead and potassium dichromate was examined with compositions that consisted of magnesium, guanidine nitrate, and metal sulfates, which had been thought to be suitable for strobe lights. From the results of experiments, examples of four colored light compositions are shown for practical use.

It is concluded that the effects of hot spots are not so clear, when using with compositions which contain usual oxidizers. However, when using with the compositions for strobe light, which do not burn so easily, the hot spot materials are very effective in adjusting the strobe reaction and to obtain the compositions in practical use.

Introduction

In the past, I studied on colored strobe light compositions for firework use.[1] At that time I could not find good compositions without ammonium perchlorate. After the work, however, I knew ammonium perchlorate is not always popular in firework fields. Therefore, I have been trying to develop new type compositions which contain no ammonium perchlorate.

The strobe light reaction is a repeating reaction of dark (smoldering) and flash (explosive burning). Figure 1 shows one cycle of the reaction. At the beginning of the cycle, the reaction is initiated by a small rest of the dark reaction zone of the former cycle. Small hot spots appear on the burning surface. The dark reaction proceeds smoldering, however, some materials are left unburned in the dark zone because of too low temperatures. A heat accumulation occurs in the dark zone with growth of the hot spots. At last, the dark zone is ignited by the hot spots to an explosive burning with a large flash. A small part of the dark zone of relatively low temperature remains on the burning surface, and it initiates the next cycle.

When the heat accumulation in the dark reaction is smaller, the growth of hot spots does not occur. Accordingly, in this case, the ignition of the dark zone does not occur, and the strobe reaction stops. Even in this case, when another heat source is used to ignite the dark reaction zone, the strobe light reaction occurs. Therefore, it may be suggested to use some hot spot

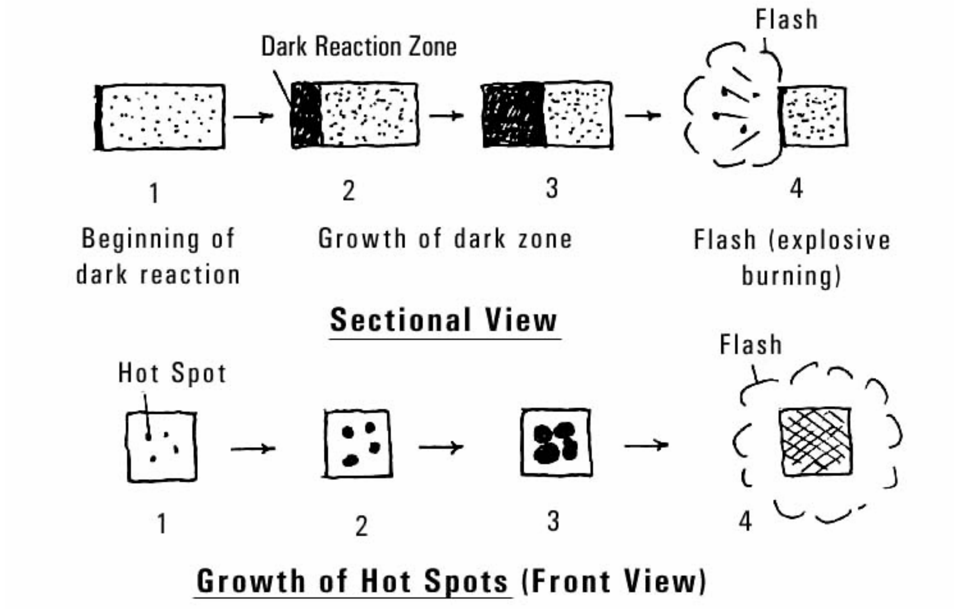

Figure 1. The principle of one cycle of strobe reaction.

materials, which locally cause high temperatures at the burning surface.

The meaning of the hot spots in this work is different from that which has usually been called with the theory of explosion or detonation.[3] We find often bright spots which are moving and glittering on the burning surface of a pyrotechnic composition. They are called here "Hot Spots."

Experiment 1. Hot Spot Materials and Their Effects on Compositions Which Contain Usual Oxidizers

Many materials, Pb_3O_4, Fe_2O_3, Fe_3O_4, MnO_2, SnO_2, S, C_2Cl_6, $K_2Cr_2O_7$, paulownia charcoal, hemp charcoal, Japanese oak charcoal, lampblack, graphite, and phenol resin etc. were examined. From these, four materials, Japanese oak charcoal, red iron (Fe_2O_3), red lead (Pb_3O_4), and potassium dichromate ($K_2Cr_2O_7$), which might be useful for producing hot spots, were selected. The grains of each material were classified into five ranks (Table 1).

Table 1. Classes of Grain Size.

Class	Mesh	Sieve opening (mm)
No. 1	14–20	1.85–1.00
No. 2	20–36	1.00–0.50
No. 3	36–60	0.50–0.22
No. 4	passed 60	0.22
No. 5	passed 200	0.074

The grains of red iron and red lead were prepared by consolidating them adding them with 4 weight percent dextrin, crushing and passing sieves.

To see the reaction properties of these materials, a sun light absorption test was carried out with the grain size of No. 3. About 0.01 grams of each material were placed on a small sheet of filter paper and put in the focus of a lens (7 cm diameter, 25 cm focus distance).[4] The waiting time of ignition was measured as follows (Table 2):

Table 2. The Waiting Time of Ignition by Sunlight Absorption Test.

Japanese oak	0.1 s
Red iron, Fe_2O_3	1.0 s
Red lead, Pb_3O_4	2.4 s
Potassium dichromate, $K_2Cr_2O_7$	3.8 s

Note: fine day, no clouds, 11:30–11:40, 9th April 1991 in Saitama-ken, Japan.

Three compositions of 18% rosin and 82% oxidizers, ammonium perchlorate, potassium perchlorate, or potassium nitrate, were prepared. 95 grams of each composition was added with 4.5 grams of each hot spot material, mixed and consolidated with a press in a paper tube in a form under a pressure of 800 kg/cm^2 to a small flare of 33 mm diameter, about 65 mm long. These sample specimens were placed vertically on the ground and ignited by using a piece of black match. However, the compositions which contained potassium nitrate were ignited not by black match, but by a powder of magnesium.

Both the groups of compositions which contained ammonium perchlorate or potassium perchlorate burned smoothly with a flat surface and a long flame. With the former, the flames were so bright that the hot spots were invisible on the burning surfaces. With the latter, the surfaces were covered by a layer of foam, and the hot spots were also invisible. With the group which contained potassium nitrate, they burned not smoothly, but very irregularly, producing molten matters, but the hot spots were clearly observed. Figure 2 shows the burning looks of the three groups.

Burning times were measured with the groups of the perchlorate, but not with the nitrate due to the very slow irregular burning. The results, including those of the base compositions of no hot spot material, are shown in Table 3.

From the results in the experiments, the influence of the hot spot materials mixed in compositions with usual oxidizers may be as follows. The potassium dichromate had the longest waiting time of ignition (Table 2). It shows that this material was not too early dissolved when being heated on the burning surface by radiation of the flame, and gave the largest influence on the burning rate. On the contrary, the Japanese oak charcoal, which had the shortest waiting time of ignition, burnt up so early that the adjacent materials were not affected to promote the burning. The effect of the red iron or red lead was between those of the potassium dichromate and Japanese oak charcoal.

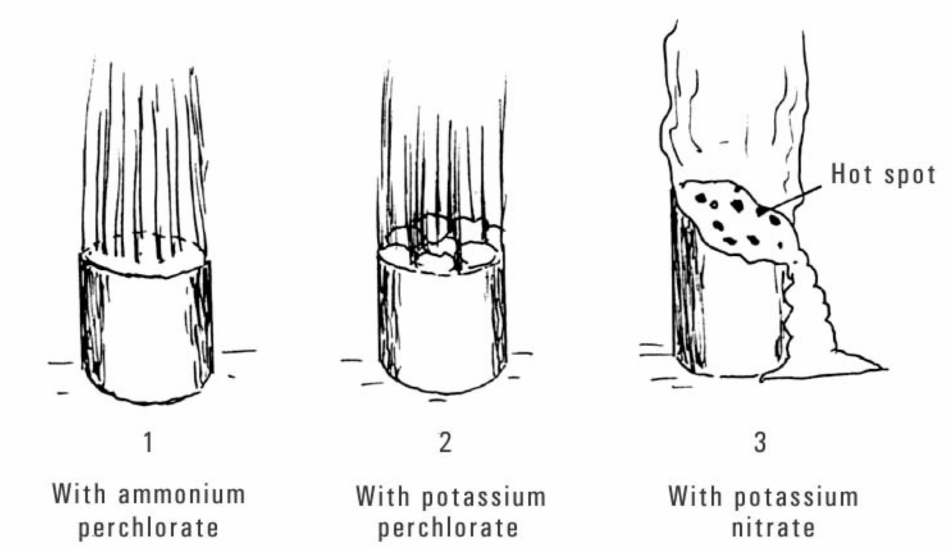

Figure 2. Burning looks of three type sample specimens.

Table 3. The Burning Rate of Compositions with Usual Oxidizers (gram/cm^2•s) with the Effect of Hot Spot Materials.

Composition	Hot Spot Material Mesh Size	Japanese Oak (5%)	Red Iron Fe_2O_3 (5%)	Red Lead Pb_3O_4 (5%)	Potassium Dichromate $K_2Cr_2O_7$ (5%)
NH_4ClO_4 + Rosin (82/18)	None	0.15	0.15	0.15	0.15
	No.1 14–20	0.15	0.14	0.15	0.14
	No.2 20–36	0.13	0.14	0.15	0.15
	No.3 36–60	0.13	0.14	0.15	0.15
	No.4 passed 60	0.16	0.15	0.15	0.19
	No.5 passed 200	—	—	0.16	0.22
$KClO_4$ + Rosin (82/18)	None	0.15	0.15	0.15	0.15
	No.1 14–20	0.15	0.17	0.15	0.17
	No.2 20–36	0.15	0.15	0.15	0.17
	No.3 36–60	0.15	0.15	0.14	0.17
	No.4 passed 60	0.17	0.17	0.15	0.19
	No.5 passed 200	—	—	0.15	—

The effects of red iron and red lead were not clear and further studied by using strobe light compositions. In experiments, the hot spots were visible only on the burning surface of compositions which contain potassium nitrate. However they burned so slow that the effect was not detected.

Experiment 2. Strobe Compositions with No Ammonium Perchlorate Using Hot Spot Materials

For preparation of strobe light compositions which contain no ammonium perchlorate, a series of burning tests was carried out by using a trigonometrical graph. The base compositions consisted of magnesium, metal sulfate, and guanidine nitrate based on a past work.[5] The sample specimens were made consolidating the three components in various ratios using a 10% nitrocellulose solution in acetone as a binder and cutting in a long rectangular form of 8 mm×8 mm×40 mm. The results are shown in Figure 3.

To obtain good colored light, 5 weight percent of chlorinated isoprene rubber was added to the base compositions. (The chlorinated rubber is a product of Asahi Denka Co. in Tokyo, and said it contains 66–67% chlorine.) Therefore, the burning characteristics denoted on the triangle were changed in some extent.

For red strobe, No. 20' was chosen as the base, for orange, yellow, or green strobe, calcium sulfate $CaSO_4$•1/2 H_2O, sodium sulfate Na_2SO_4, or barium sulfate $BaSO_4$ was substituted respectively for the strontium sulfate. The burning characteristics were somewhat changed from those on the triangle due to the substitution of the sulfates. For orange strobe, however, No. 20' was chosen as the base. For yellow strobe, No. 20' was also chosen as the base, however, the chlorinated rubber was omitted, because it is unnecessary for emission of sodium light. For green strobe, No. 28' was chosen rather largely changing from No. 20'.

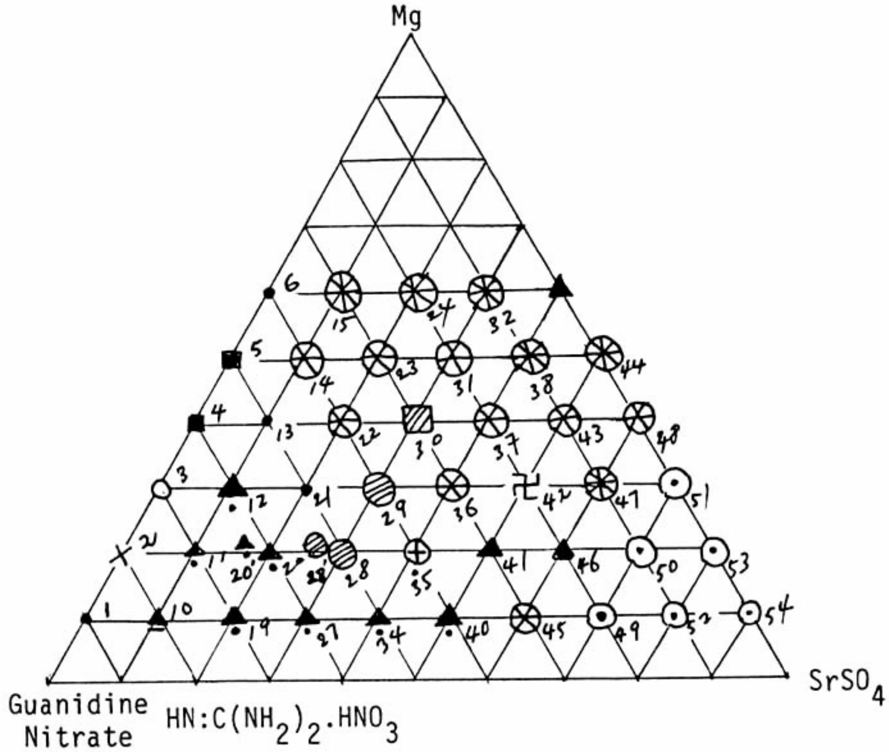

Figure 3. Burning characteristics of base compositions of strobe light.

Symbols:	●:	Only smolders.	⊗:	Continuous burning.
	○:	Only burns.	⊛:	Continuous and intensive burning.
	■:	Very slowly blinks.	[hatched circle]:	Blinks with a large flame.
	⬩:	Blinks not sharply.	[hatched square]:	Blinks without sharp cut.
	[▲ with underline]:	Irregularly blinks.	⊕:	Burns, then smolders.
	[▲ with dot]:	Blinks, then smolders.	⊙:	Burns with small flame.

Adding the hot spot materials to the base compositions, about seventy burning tests were carried out by a process of trial and error. The results are shown in Table 4.

These compositions were added with a weight of 10% nitrocellulose solution in acetone and consolidated into 8 mm cubic cut stars.

Table 4. Examples of Colored Light Strobe Compositions.

	Ingredient	Red	Orange	Yellow	Green
Base composition	Magnesium, Mg	18.3%	18.3%	19.9%	17.5%
	Guanidine nitrate, $HN:C(NH_2)_2 \bullet H_2O$	54.6	54.6	59.8	52.8
	Chlorinated isoprene rubber	4.5	4.5	—	6.1
	Strontium sulfate, $SrSO_4$	13.6	—	—	—
	Calcium sulfate, $CaSO_4 \bullet 1/2H_2O$	—	13.6	—	—
	Sodium sulfate, Na_2SO_4	—	—	15.0	—
	Barium sulfate, $BaSO_4$	—	—	—	13.2
Hot spot material	Red lead (fine powder, No. 5)	4.5	4.5	0.3	6.1
	Potassium dichromate (Grain size No. 3, passing 36–60, did not contain fine powder)	4.5	4.5	5.0	4.0
	Strobe frequency (Hz) of 8 mm cubic cut star	1.10	ca 1.0	ca 0.7	ca 0.6

For ignition of the stars, following composition was used (Table 5).

Table 5. An Ignition Composition for the Strobe Stars of the Compositions in Table 4.

Magnesium passing 100 mesh	35 %
Cupric oxide, CuO	65 %

The stars were sprinkled with this ignition composition once or twice using the nitrocellulose solution as a binder.

Through the tests, it became clear that red lead creates one cycle of strobe reaction (smoldering and flashing) and potassium dichromate connects the cycle with the next cycle without stopping. When no red lead was used, the compositions burnt only continuously and slowly. The grain or particle size of the red lead must be fine; when large, the compositions also continuously burnt. When a small quantity of red lead of fine grains or particles was added to the composition, they blinked but the reaction went out with an explosive noise. When a small quantity of the potassium dichromate was added to these compositions, they blinked repeatedly without extinction. The grain size of the potassium dichromate must be somewhat large and must not be fine. When a fine powder was used, the compositions burnt only continuously.

The size of stars which are made of such a type of composition must not be so large to obtain a good strobe effect. When too large, the burning reaction is stabilized by the effect of hot spots to cause no strobe reaction. In this experiment, it was shown that an 8 mm cube might be the maximum size of the star.

Discussion and Conclusion

Four materials were chosen as a hot spot creating material. The grains of them were sieved into five classes.

They were examined by a sunlight absorption test, and from the results the order of reactivity as hot spots may be arranged as follows:

Japanese oak charcoal > Red iron > Red lead > Potassium dichromate.

Five additional percent of each material was mixed into compositions of three types: rosin + ammonium perchlorate, rosin + potassium perchlorate, and rosin + potassium nitrate. With test specimens of the former two, the burning rate was measured; the larger the reactivity, the smaller the influence. When using the charcoal, its grains instantaneously burnt up and the reaction did not affect the dissociation of the adjacent materials. On the contrary, using potassium dichromate, its grains on the burning surface dissolves rather slowly, and it could take part in the burning reaction. Anyhow, the reaction of hot spot grains should match that of the adjacent materials on the burning surface.

The grain size of the hot spot materials had a relatively large effect on the burning rate of the composition; the smaller the grain size, the larger the burning rate. This may be due to the number of the hot spots on the burning surface; the larger the number, the larger the rate. The composition of rosin and potassium nitrate so irregularly burnt that their data of the effect could not be obtained, although the spots were clearly observed.

Further, the hot spot materials were added to compositions for strobe use, mixtures of magnesium, metal sulfate, and guanidine nitrate, etc., which are somewhat unstable in burning. These compositions often smolder with a dark reaction zone. In the zone heat accumulation is not large enough to cause the ignition of the dark zone itself. Therefore, to produce a good strobe light, it should be helped by adding some hot spot material to cause the ignition of the dark zone.

As the hot spot materials, red lead and potassium dichromate were used considering the lives on the burning surface might not be so short. At last, relatively good strobe light compositions for red, orange, yellow, and green colors were obtained (Table 4). In this case, red lead helped the dark reaction and the ignition of the dark reaction to a flash, however, the reaction is cut out by the flash. To avoid the stop of the reaction, the potassium dichromate was added. The grain size of the red lead must be very fine; on the contrary, that of potassium dichromate must be coarse in some extent.

The hot spot materials are effective for compositions which do not easily burn as strobe compositions, and may not be so effective for those which burn easily, except some substances like potassium dichromate.

The stars of strobe compositions of this type should not exceed 8 mm cube in dimension to avoid continuous burning.

Reference

1) T. Shimizu, "Studies on strobe light pyrotechnic compositions", *Pyrotechnica VIII* (1982) p 5.

2) *ibid*. p 27.

3) F.P. Bowden and A.D. Yoffe, *Initiation and Growth of Explosion in Liquids and Solids*, Cambridge at the University Press, 1952.

4) T. Shimizu, *Feuerwerk vom physikalischen Standpunkt aus*, Hower Verlag, Hamburg, 1976, p 5.

5) *ibid*. with (1), p 18.