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CAUTION

The experimentation with, and the use of, pyrotechnic materials can be dangerous; it is felt to be important for the reader to be duly cautioned. Anyone without the required training and experience should never experiment with nor use pyrotechnic materials. Also, the amount of information presented in these articles is not a substitute for the necessary training and experience.

A major effort has been undertaken to review this text for correctness. However, it is possible that errors remain. Further, it must be acknowledged that there are many areas of pyrotechnics, fireworks in particular, for which there is much “common knowledge”, but for which there has been little or no documented research. Some articles herein certainly contain some of this unproven common knowledge. It is the responsibility of the reader to verify any information herein before applying that information in situations where death, injury, or property damage could result.

CREDITS

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Dr. Takeo Shimizu

In the evening at half past seven o'clock an old man came back from his duty work of the day with a sound of gravel to the wooden gate. The winter sun already set, and one could barely see him through the darkness. His head was not so gray, but his steps looked somewhat unsteady. He passed and closed the gate with a light noise and pushed the doorbell. His wife opened the front door. She looked very cheerful, but hunchbacked owing to the break of her backbone several years ago. After taking supper, he fell asleep in his seat. His room has been recently confused. The book-shelves are full of books. There stand the complete works of Dr. Nishida and Dr. Tanabe on philosophy, books concerning Buddhism and the complete works of Kenji Miyazawa on poets. Testaments in various languages and the Arabic Koran are also on the shelves. They are covered in dust and will sleep until he has more time. When his wife was in good health before the injury, several persons in overseas countries stayed nights in his house; however, it has become impossible.

Dr. Takeo Shimizu was born in 1912 in a small village Takamata in Yama-guchi Prefecture which is in the middle of Japan. His father was farmer. He had a rather long student life from 1929 to 1940: four years of middle school in Hagi, four years and ten months at the Military Academy on the Ichigaya-Hill in Tokyo, two years at the Artillery and Engineer Academy in Wakamatsu-Cho Tokyo, three years at Tokyo University (Faculty of Explosives) to which he was dispatched from the Military. He did also during the period the duty work for one year and a half at the Saseho Heavy Artillery Regiment and was trained as an Artillery Officer.

From 1940 to 1945 he worked as a member of the Second Military Ordnance. He experienced manufacturing nitric acid, nitrocellulose, tetryl, TNT, smokeless powder, etc. In 1942 he had an additional post as the teacher at his Alma Mater, the Artillery and Engineer Academy and gave lectures on interior ballistics to young officers in the higher course. When War II was over in 1945, he was lieutenant colonel and the leader of the ballistics section of the Institute of Explosives of the Ordnance.

One day in the autumn of 1951, when he was working as a farmer in his hometown Takamata, he received a letter from Professor S. Yamamoto, his former teacher of the Faculty of Explosives in Tokyo University. Dr. Yamamoto recommended him to study Hanabi (Fireworks). He did not know anything about fireworks, but felt it might be very interesting and accepted Dr. Yamamoto's request. This was the chance of his working as a pyrotechnist.

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(Biography of Dr. Shimizu – continued from back of Title Page)

Dr. Yamamoto further asked him to reduce accidents in the firework field and to make the traditional technique more scientific. Through the introduction of Dr. Yamamoto he obtained a position at Hosoya Fireworks Co. in Tokyo in November 1951. In many cases of experiments hereafter he used Terada's Method. The late Dr. Terada (1875–1935) was a famous professor in the Faculty of Physics in Tokyo University. The method might be simply said: "Don't use noble instruments, but use the human head". Professor Nakaya succeeded to make clear the crystallization mechanism of snow following faithfully this method. Mr. M. Hosoya very kindly taught his secrets of firework technique called "Machida School". He analyzed the technique of Japanese chrysanthemum shells and Dr. Yamamoto recommended that he submit the paper as a thesis for a degree. In 1958 he was granted the degree of Doctor of Engineering with the paper "The Design Conditions of Chrysanthemum Shells".

His senior, A. Kawai asked him to help with his work, the manufacturing of rocket propellants at the plant of Dainippon Celluloid Co. in Kochi village in Hyogo-ken. He often visited the plant and designed rocket propellant. In 1963 he changed his position to the Perfect Liberty Religion Order in Osaka accepting the offer from the founder, T. Miki, who planned to build a new factory and an institute of fireworks; however, the plan was not realized because of financial reasons.

In 1967 he got his present position in the factory of Koa Fireworks Co. in Hidaka-shi Saitama-ken. The factory was built by his old friend, the late N. Mizogami, who built a small laboratory for him. The factory was mainly producing maritime distress signals. He is continuing the study of fireworks finding time intervals, even now, following the request of the old teacher, the late Dr. Yamamoto.

When he was still young, however, he made effort to learn for himself fundamental physics, languages, religions and philosophy. He was especially deeply moved by Buddhism. He understood its doctrine using a simile as: "The world is like a broken beaker having a hole at the bottom. The water level in it falls down and down when man makes no effort to draw up the water. Don't be idle!" In 1955 he dramatized this opinion which concerns the primeval Buddhism and wrote to a magazine *Zen* published by Mr. Murase, the late superintendent priest of Temple Obakusan in Uji. The Zen in Buddhism was also understood by him as: "See things direct without prejudice!" He had thought on the theory of relativity: the time axis of the space ict must come from a geometrical average of a past time $-t$ and the corresponding future time $+t$ as $ict = c \times \sqrt{(-t) \times (+t)}$. For this noesis the professors gave him neither a positive nor negative response, but the late Mr. Iwama, a friend of ballistics, alone, supported him.

At present he is thinking through the experiences of pyrotechnics field that chemical theories at present must be rewritten. Because, the theories originally came from separable molecules of gas or dilute solutions of materials. Pyrotechnists treat in general solid or concentrated solutions of materials. He is making an effort to establish a theory using the idea of the theory of set mathematics.

In his works on fireworks and pyrotechnics he sets always practice and originality before others. He meets almost every day new and difficult problems. He applies the method of Zen to such cases. He doesn't like aimless lifting of shells. His special invention, which gave people a great inspiration, was an 18-inch daylight chrysanthemum shell, which was named "Evening Glory of Sunset". There appear firstly various thick colored lines of smoke. When they fully spread as petals, suddenly appears a pistil of dazzling flashes of magnesium red on them.

Originally appeared in *Proceedings of the 10th International Pyrotechnic Seminar*, July, 1985.

Hypothesis on the Cause of Serious Accidents Related to Salutes Charges

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ABSTRACT

First, we hypothesize that a serious accident related to the use of salutes may be caused by the simultaneous explosion of several salutes or salute components, resulting in an unexpected, abnormally strong shock wave. To prove our theory, we conducted three experiments. In Experiment 1, we examined the transfer of the explosion between salutes with one donor to shed light on the properties of the charges. Experiment 2, which we conducted to examine the transfer in the case of two donors, revealed a localized effect of the transfer. In Experiment 3, we measured the pressure during explosion using a pressure-sensing film, which was used to create pressure contour lines. Our experiments reveal that there is an area of abnormally high pressure, a finding which supports our hypothesis.

1. Introduction

Pyrotechnic salutes are generally very susceptible to mechanical stress. To prevent accidents when handling and storing them, two methods are commonly used: dividing a charge into as many small pieces as possible and isolating each partial charge using appropriate methods, such as placing parts at a distance from one another and separating them up or enclosing them. The reasoning behind this approach is that, even if one of the salute components were to explode somehow, no serious accident would result. Yet, in the past, the occasional accident has been encountered for which no clear cause could be determined, since it was always difficult to recreate any of the accidents under experimental conditions.

One hypothesis is that a serious accident can occur when just two salute components (or more) explode at the same time. This creates an unexpected, strong shock wave, as I will explain in an experimental context below. Due to a chain reaction occurring among the components, the shock wave will be transferred to all the charges.

2. Experiment 1

We used the following common Japanese salute formulations:

A:	potassium perchlorate	64%
	aluminum (300 mesh flakes)	23%
	sulfur	13%
B:	potassium chlorate	64%
	aluminum (300 mesh flakes)	23%
	sulfur	13%
C:	potassium chlorate	57%
	realgar (As_2S_2)	43%

The individual charges were represented by spherical or cylindrical salutes as shown in Figure 1. Each salute, with the exception of a few, contained an explosive charge of 25 g of either A, B or C, enclosed in a hard paper shell casing, with a charge density of 0.65 g/cm^3. Depending on the requirements, the thickness of the hard paper shell casing ranged from 0.7 to 4 mm. Occasionally, a piece of steel pipe with an inner diameter of 28 mm and a thickness of 1 mm was used for the cylindrical salute (Figure 1).

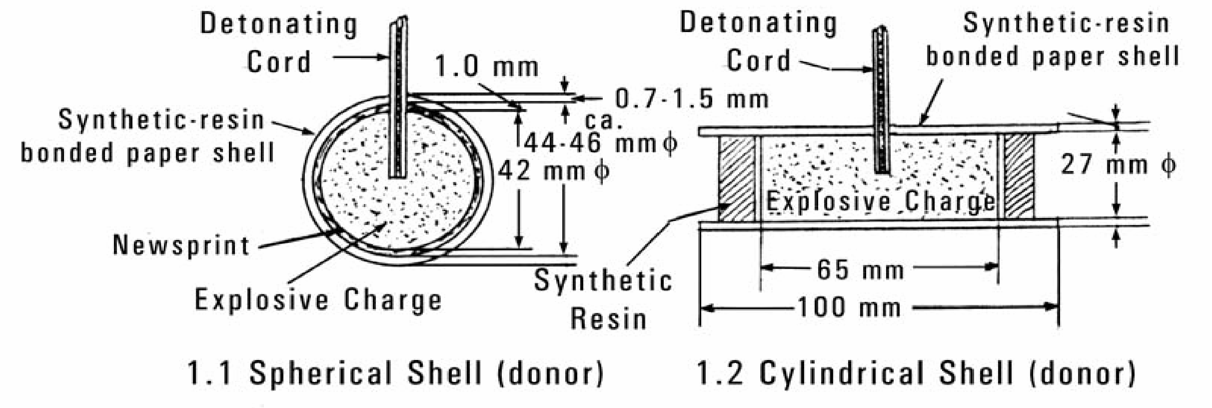


Figure 1. Samples used as partial charges.

Three identical salutes were each suspended 35 cm from a horizontal steel rod using 0.7 mm thick steel wire so as to hang in a horizontal line, about l m above the ground, at an equal distance of 0–4.4 D from each other, D being the diameter of the salute. The first salute, which was used as the donor, contained an igniter (detonating cord with an electric detonating cap, an electric igniting primer or quick match) (Figures 2.1 and 2.2). The donor was ignited and the transfer of the explosion from A to B and then to C was examined. The results are shown in Table 1.

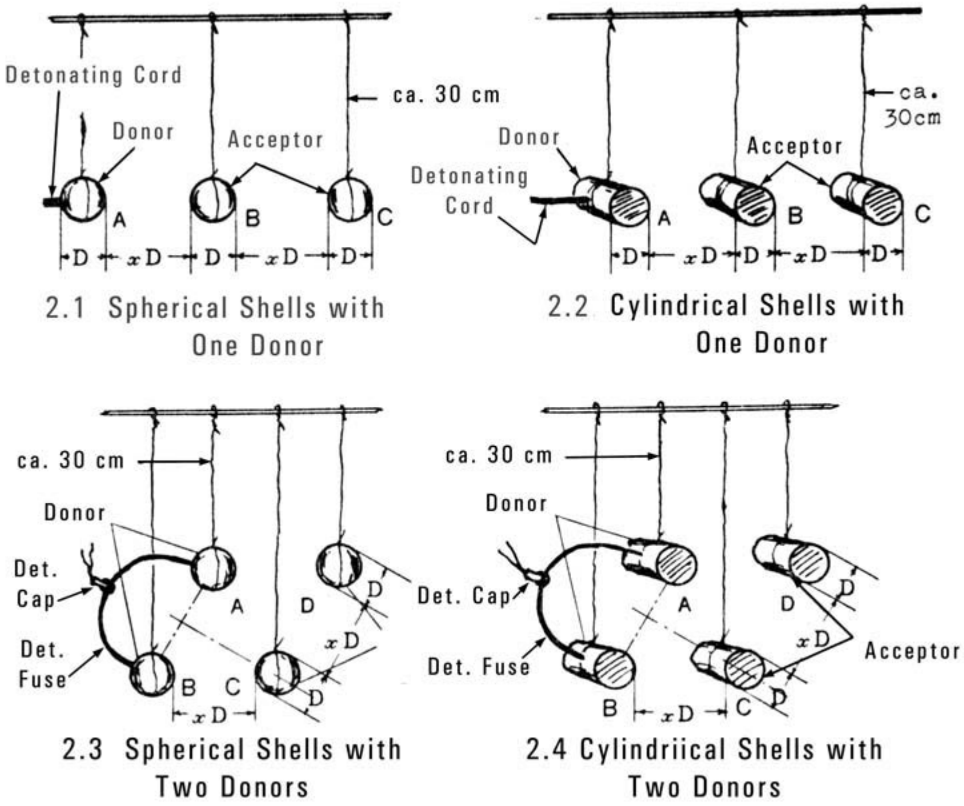


Figure 2. Assemblies for transfer experiments.

The results show that the transfer effect of the first salute (the donor) is much greater than that of the second, if detonating cord is used to ignite the donor. In reality, an accident would happen differently, since this type of igniter would not actually be used in practice. However, to make two salutes explode simultaneously, as done in the experiments described below, Detonating cord had to be used.

3. Experiment 2

Four identical salutes were suspended on 0.7 mm thick steel wire from a steel rod and arranged in the shape of a rectangular parallelogram (Figures 2.3 and 2.4). Salutes A and B were used as donors. They were attached to each other with a piece of detonating cord. A detonating cap was attached at the center of the detonating cord, so as to ensure that A and B would explode simultaneously.

The two donors were ignited and the transfer of the explosion from A and B to C and D was examined. The results are recorded in Table 2. They show that the effect of the shock wave is much stronger at location C than at location D, because each salute at location C (with the exception of sample 24, for which the spacings were very wide) exploded, while none (with the exception of sample 25) exploded at location D. We also provided a few additional results in Table 3.

Table 1. Results of Transfer Tests Using Three Identical Salutes with One Donor.

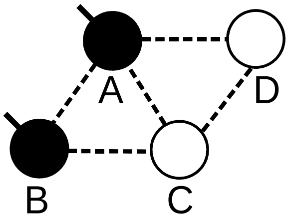
Charge per shell: 25 g –●A—○B—○C

No.	Charge	Shell			Space between (mm)	Igniter	A	B	C
		Shape	Material	Thickness (mm)					
1	A	Spherical	Hard paper	1.5	115 (2.5D)	cap and cord	–●	●	○
2	A	Spherical	Hard paper	1.5	92 (2D)	cap and cord	–●	●	○
3	A	Spherical	Hard paper	1.5	46 (1D)	cap and cord	–●	●	○
4	A	Spherical	Hard paper	1.5	0	cap and cord	–●	●	○
5	A	Spherical	Hard paper	1.5	92 (2D)	igniting primer	–●	○	○
6	A	Spherical	Hard paper	1.5	69 (1.5D)	igniting primer	–●	○	○
7	A	Spherical	Hard paper	1.5	46 (1D)	igniting primer	–●	○	○
8	A	Spherical	Hard paper	1.5	23 (0.5D)	igniting primer	–●	○	○
9	A	Spherical	Hard paper	1.5	0	igniting primer	–●	●	○
10	A	Spherical	Hard paper	1.5	0	quick match	–●	●	○
11	A	Spherical	Hard paper	0.7	50 (1.1D)	cap and cord	–●	●	○
12	B	Spherical	Hard paper	0.7	100 (2.2D)	cap and cord	–●	●	●
13	B	Spherical	Hard paper	1.5	200 (4.4D)	cap and cord	–●	○	○
14	C	Spherical	Hard paper	0.7	100 (2.2D)	cap and cord	–●	●	○
15	C	Spherical	Hard paper	1.5	100 (2.2D)	cap and cord	–●	○	○
16	A	cylindrical	Hard paper	0.5	29 (1D)	cap and cord	–●	●	●
17	A	cylindrical	Hard paper	1.0	29 (1D)	cap and cord	–●	●	●
18	A	cylindrical	Hard paper	2.0	29 (1D)	cap and cord	–●	●	◐
19	A	cylindrical	Hard paper	4.0	29 (1D)	cap and cord	–●	○	○
20	B	cylindrical	Hard paper	2.0	29 (1D)	cap and cord	–●	●	●
21	C	cylindrical	Hard paper	2.0	29 (1D)	cap and cord	–●	●	●
22	A	cylindrical	Iron	1.0	30 (1D)	cap and cord	–●	○	○

Notes: –● = donor with igniter
● = acceptor which exploded
◐ = acceptor only half of which exploded
○ = acceptor which did not explode
D = outer diameter of shell

Table 2. Results of Transfer Tests Using Four Identical Salutes with Two Donors Ignited Simultaneously.

Explosive charge per shell: 25 g
Shell: Shape: Spherical
Material: Hard paper casing
Thickness: 1.5 mm
Igniter: Detonating cap and cord

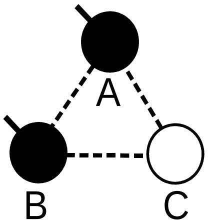


No.	Charge	Space between (mm)	Results A	 B	 C	 D
23	A	74 (1.6D)	-●	-●	●	○
24	A	140 (3D)	-●	-●	○	○
25	A	74 (1.6D)	-●	-●	●	●
26	A	118 (2.5D)	-●	-●	●	○
27	A	118 (2.5D)	-●	-●	●	○

Note: The symbols are the same as in Table 1.

Table 3. Results of Transfer Tests Using Three Salutes with Different Explosive Charges and Two Donors Ignited Simultaneously.

Shell: Shape: Spherical
Material: Hard paper casing with thickness: 1.5 mm



No.	Charge	Space between (mm)	Igniter	Charge per Firecracker & Result A	 B	 C
S1	A	300 (6.5D)	cap and cord	25 g -●	25 g -●	15 g ○
S2	A	100 (1.8D)	cap and cord	25 g -●	25 g -●	15 g ●
S3	A	100 (1.8D)	cap and cord	15 g -●	15 g -●	15 g ●
S4	A	100 (1.8D)	cap and cord	10 g -●	10 g -●	10 g ○
S5	A	100 (1.8D)	igniting primer	25 g -●	25 g -●	15 g ○

Notes: The symbols are the same as in Table 1.
When the igniting primers were used, the two donors likely did not explode simultaneously.

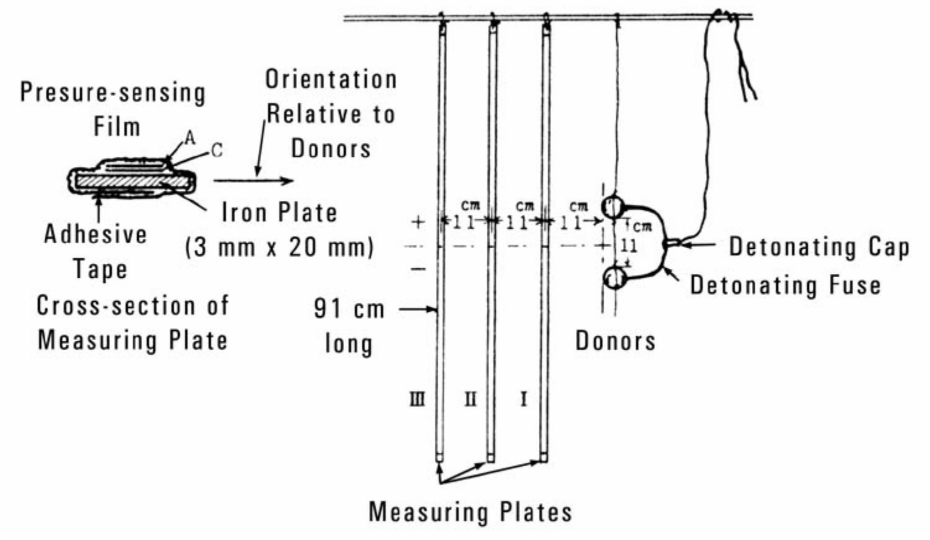


Figure 3. Pressure-measuring assembly.

4. Experiment 3

To explain the propagation of pressure from the two donors, we measured the pressure using a pressure-sensing film (Prescale) from Fuji Film Co. When pressure is exerted on the film, microcapsules burst and color the film red. The pressure is measured by measuring the density of the coloration. The film consists of two films, A and C. A is 0.105 mm thick and contains a layer of microcapsules. C is 0.095 mm thick and contains a color-producing layer. The films were cut into 10 mm-wide strips and both layers placed onto a 3 mm-thick, 20 mm-wide and 91 cm-long steel plate. This assembly was covered with cloth adhesive tape to prevent destruction by the explosion (Figure 3, left). The pressure-measuring assembly is shown in Figure 3.

Ignition of the donors resulted in the red coloration of the strips, as shown in Figure 4. The density of the coloration was measured using a Fuji FPD201 density-measuring device, the latter also indicating the pressure directly (Figure 7). Figures 5 and 6 show examples of pressure contour lines, which were drawn by the pressure, assuming that the pressure is continuous. This method does not explain how pressure develops in a given area; all it indicates is maximum pressure over time. Pressure in the shaded area is 50 kg/cm^2 and more.

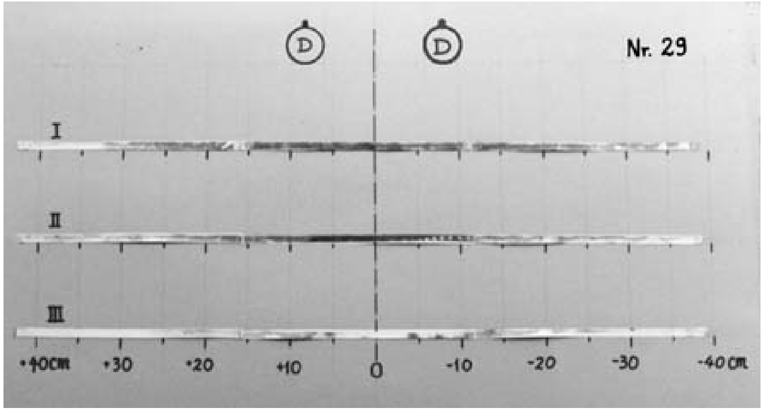
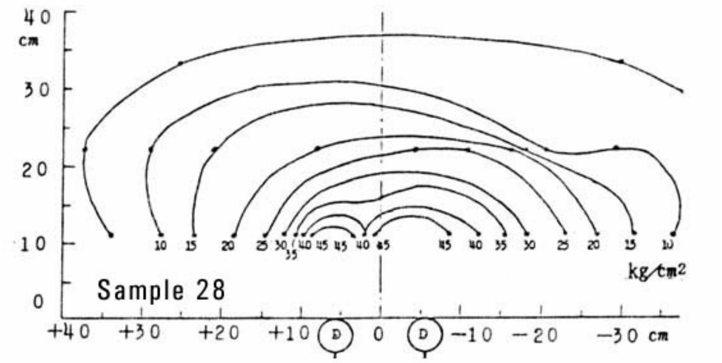
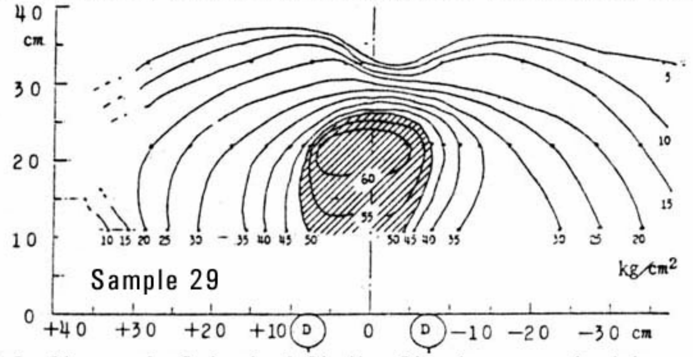


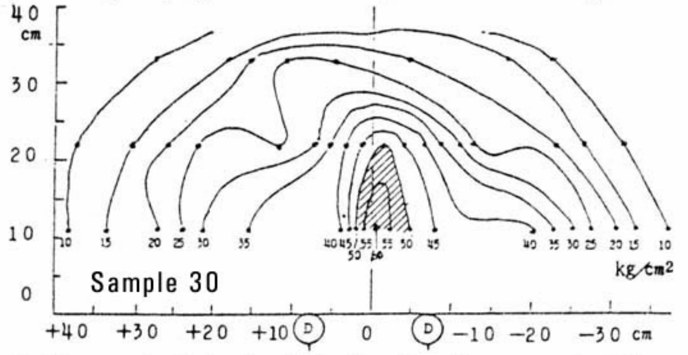
Figure 4. Coloration of pressure-sensing films (sample 29).



5.1 Charge A, Spherical Shells, Ignited at Different Times

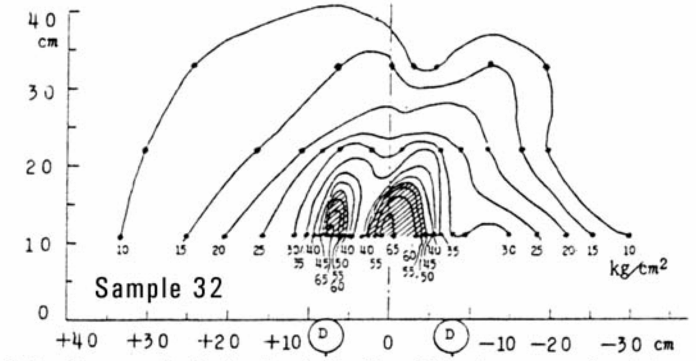


5.2 Charge A, Spherical Shells, Simultaneous Ignition

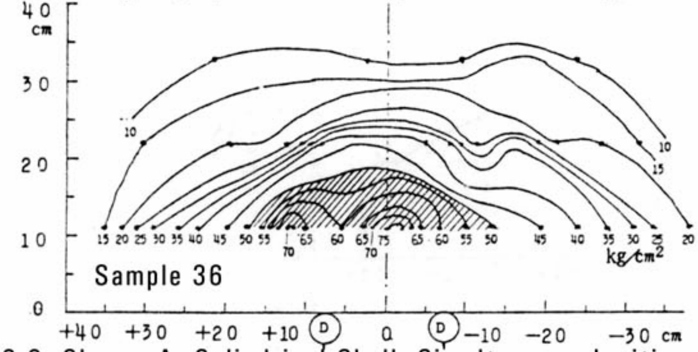


5.3 Charge A, Spherical Shells, Simultaneous Ignition

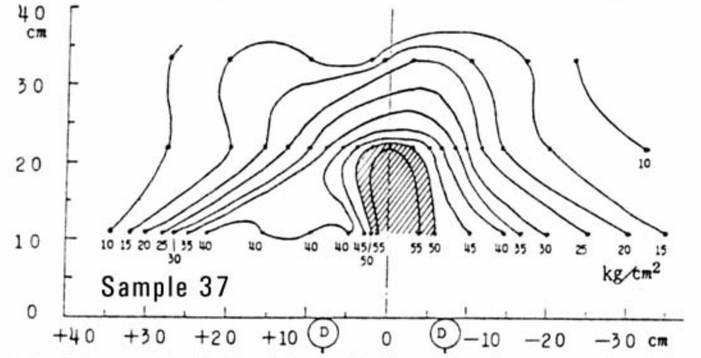
Figure 5. Pressure propagation upon explosion of dual donors (I).



6.1 Charge B, Spherical Shells, Simultaneous Ignition



6.2 Charge A, Cylindrical Shell, Simultaneous Ignition



6.3 Charge B, Cylindrical Shells, Simultaneous Ignition

Figure 6. Pressure propagation upon explosion of dual donors (II).

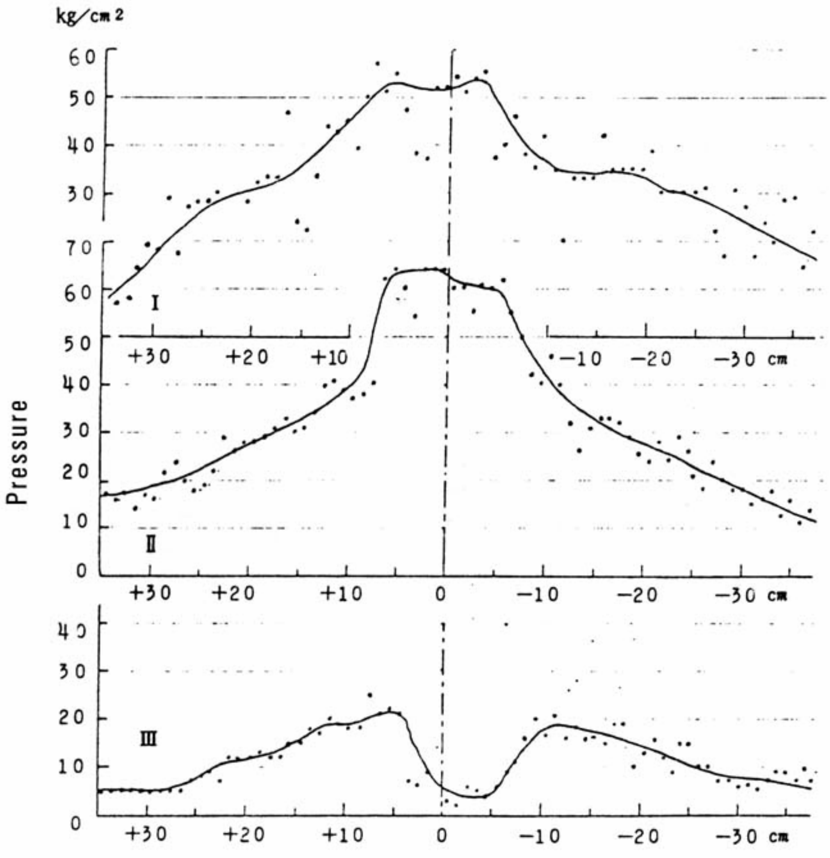


Figure 7. Reading of pressure as indicated by the coloration of the pressure-sensing films, using a Fuji FPD201 density-measuring device (sample 29).

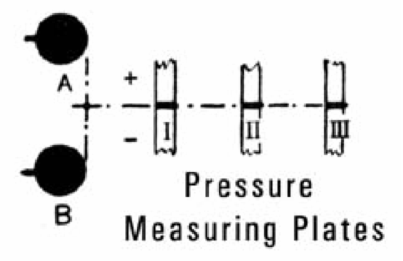
5. Discussion

It seems that the transfer effect of the donor having the detonating cord is not equally strong in all directions, but one-sided in the direction of the detonating cord (Figure 5.1). As previously mentioned, use of the detonating cord was necessary, in order to be able to explode the two donors simultaneously.

When the two donors were not ignited simultaneously, the maximum pressure in their vicinity was lower, and it soon weakened (Figure 5.1 and Table 4). However, when the two donors were ignited simultaneously, a very high pressure resulted along the axis (Figures 5.2 and 5.3; Table 4). This may be caused by the fact that the shock waves from the two donors collide with one another. We therefore think that the simultaneous explosion of two or more salutes or salute components of an explosive charge may cause a chain reaction, resulting in a serious accident. In terms of the shape of the salute, it seems that the transfer effect of the cylinder is greater than that of the sphere, since the maximum pressure of the former was generally higher than that of the latter (Tables 1 and 4). The thickness of the shell also influences the transfer effect (samples 16–19 and 22 in Table 1). The thicker the shell, the weaker the effect.

Table 4. Results of Tests Measuring Pressure in the Case of Dual Donors.

Explosive charge per shell: 25 g
Shell: Material: Hard paper casing
Thickness: Nos. 28–34: 0.7 mm
Nos. 35–39: 1.0 mm
Space between salutes:
No. 28: 66 mm (1.5D)
Nos. 29–30: 110 mm
D = 44 mm (outer diameter of shell)
Ignition: Detonating Cap and Cord



				Maximum Pressure					
				I		II		III	
No.	Charge	Shell Shape	Ignition	Press. kg/cm^2	Loc. cm	Press. kg/cm^2	Loc. cm	Press. kg/cm^2	Loc. cm
28	A	Spherical	Not Simultaneous	52	–6	30	–8	11	0
29	A	Spherical	Simultaneous	57	+8	64	0	25	+7
30	A	Spherical	Simultaneous	60	0	50	0	41	+5
31	A	Spherical	Simultaneous	65	+3	52	+2	18	+13
32	B	Spherical	Simultaneous	66	–2	44	+3	21	+2
33	B	Spherical	Simultaneous	57	–5	22	–8	8	+2
34	C	Spherical	Simultaneous	33	+7	22	–8	19	0
35	A	Cylinder	Simultaneous	76	+8	47	–7	29	+5
36	A	Cylinder	Simultaneous	76	–2	56	+7	15	+16
37	B	Cylinder	Simultaneous	68	–3	55	0	30	0
38	B	Cylinder	Simultaneous	68	0	48	–	35	–2
39	C	Cylinder	Simultaneous	19	+3	22	0	17	+6
40	for none of the detonators, except in the case of the detonating cap and cord			10	+2	—	—	—	—

6. Summary

By carefully testing salutes for their transfer effect and measuring the propagation of the pressure created during the simultaneous explosion of two donors, we determined that an area of abnormally high pressure is produced. This is likely due to the collision of the shock waves created by the two donors. However, in reality, this scenario is rather unlikely, since the possibility that several salutes or salute components will explode at the same time is rather low. Still, it must be ensured that salutes are handled, stored and safety-tested properly.

Originally appeared in *Proceedings of the 11th International Pyrotechnics Seminar,* July 1986.

A Concept and the Use of Negative Explosives

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ABSTRACT

In general, a pyrotechnic composition consists of an oxygen donor such as KNO_3, $KClO_3$, or $KClO_4$, etc., an oxygen donee such as organic resin and some other inert substances. When substances, $CaCO_3$, Al_2O_3, SiO or $CaSO_4$, etc. are contained in it, they are regarded as an inert substance, because they are full of oxygen and cannot be more oxidized. This type of explosive deflagrates with oxidation reaction and could be called "positive explosives". However, when some substances, Mg, Al or Si, etc., which have a very large reduction capacity, the inert substances change to active ones. This type of explosives, which consist of Mg, Al or Si, etc., plus a substance which is thought to be inert in conventional explosives, is defined here as "negative explosives".

With the oxygen donee, Mg was concerned as a representative case, because it is very popular and has the largest reduction capacity; it burns even sand or earth.

About 50 types of negative mixtures were listed as samples. Their characteristics were examined by several tests. Ignition and burning properties were tested on the ground by using black match. Ignition temperatures were obtained from a heating test in a glass tube. Illuminating capacities were measured by burning consolidated mixtures as a flare. Ballistic characteristics were examined by firing a projectile with a small mortar by using granulated mixtures for the propellant charge.

The results were discussed and a proposal for use of negative explosives was made.

Introduction

A new concept might rouse us to new discoveries or inventions from very common materials. Therefore, I propose here a concept of the "negative explosives".

In general, a pyrotechnic mixture consists of an oxygen donor such as KNO_3, $KClO_3$, $KClO_4$ or NH_4ClO_4, etc., an oxygen donee such as charcoal or organic resin and some other inert substances. When substances such as $SrCO_3$, $CaCO_3$ or $Na_2C_2O_4$, etc. were contained in it, they are regarded as an inert substance, because they are full of oxygen and cannot be more oxidized. This type of explosive deflagrates with oxidizing reaction only of the oxidizer, and it could be called the "positive explosive" or "positive mixture". However, when some substances such as Mg, Al or Si, etc. are used as an oxygen donee, the inert substances change to active ones as an oxygen donor. This effect introduces the new type of explosives.

The "negative explosive" or "negative mixture" is a mixture which mainly consists of an oxygen donee such as Mg, Al or Si, etc. plus substances which contain O, Cl, or F and which are not used as an oxygen donor for ordinary positive explosives. Of course some other substances may be added to it for purposes**.** This type of explosive deflagrates with a large reduction capacity of the oxygen donee.

In this report, only Mg is concerned with the oxygen donee as a representative case, because Mg is very popular and it has the largest reduction capacity: it burns even sand or earth. The name of a mixture is called here by the name of the substance which is to be mixed with Mg.

Preparations for Experiments

The mixing ratio of Mg to another substance in each two component mixture was determined by the theoretical reaction formula with few exceptions. For example:

$H_2O + Mg \rightarrow MgO + H_2$
(l g H_2O : 0.742 g Mg)
$SrCO_3 + 3\ Mg \rightarrow Sr + C + 3\ MgO$
(l g $SrCO_3$: 0.495 g Mg)
$SrSO_4 + 5\ Mg \rightarrow Sr + MgS + 4\ MgO$
(l g $SrSO_4$: 0.662 g Mg)
$Mg_3(Si_4O_{10})(OH)_2$ + l7 Mg $\rightarrow 4\ Mg_2Si +$
$12\ MgO + H_2$
(l g talc : 1.089 g Mg)

When the substance was not clear in the chemical formula as with a glass powder or earth (clay), a weight ratio of 1:1 was used for the components. A special case with water and Mg, the composition had to change from the theoretical formula, because the mixture was modified by adding small quantities of $K_2Cr_2O_7$ and starch to avoid the corrosion of the Mg and to gelatinize the mixture. The additive material for coating Mg, a binder, or some other impurities were neglected in the calculations. Table 1 shows the results.

The Mg for a heating test passed 60 mesh. The Mg for other tests was analyzed as 30–38 mesh: 9.2%, 38–48 mesh: 52.7%, 48–80 mesh: 36.0%, smaller than 80 mesh: 2.l%. The latter was coated with an additional 4% of linseed oil. Other substances which were mixed with Mg were first class powdered reagents except some items such as talc, glass powder or clay, etc.

The mixtures used for a ballistic test were granulated adding an additional 10% of 10% nitrocellulose solution in acetone and passing through a 20 mesh sieve to effect an instantaneous surface ignition.

Table 1. A List of Negative Mixtures.

No.	Substance mixed with Mg	Equivalent weight of Mg (g)	Specific gravity (g/cc)	Hazard Properties		
				by heat	by impact	Ash with water
1	Blank	1.000	—	x	x	x
2	H_2O	0.742	1.27	x	x	x
3	Li_2CO_3	0.988	1.47	x	x	ignited
4	Na_2CO_3	0.698	1.42	x	x	ignited
5	$NaHCO_3$	0.868	1.60	x	x	ignited
6	K_2CO_3	0.528	—	x	x	—
7	$CaCO_3$	0.729	1.75	x	x	ignited
8	$SrCO_3$	0.495	2.07	x	x	x
9	$BaCO_3$	0.531	1.98	x	x	x
10	$CuCO_3{:}Cu(OH)_2$	0.550	1.68	x	x	ignited
11	$Na_2C_2O_4$	0.832	1.74	x	x	ignited
12	$CaC_2O_4{\bullet}H_2O$	0.832	—	x	x	—
13	SrC_2O_4	0.554	1.70	x	x	—
14	Na_2SO_4	0.856	1.67	x	x	—
15	K_2SO_4	0.686	1.71	x	exploded	—
16	$MgSO_4$	0.808	1.45	detonated	sparked	x
17	$CaSO_4{\bullet}1/2H_2O$	0.922	1.64	exploded	x	ignited
18	$SrSO_4$	0.662	2.19	exploded	x	x
19	$BaSO_4$	0.521	2.19	x	exploded	ignited
20	$Al_2(SO_4)_3{\bullet}18H_2O$	1.214	—	x	x	x
21	$FeSO_4{\bullet}7H_2O$	1.050	1.44	x	sparked	x
22	$CuSO_4$	0.762	—	exploded	x	—
23	$NiSO_47H_2O$	1.039	—	x	x	x
24	$(NH_4)_2SO_4$	0.920	—	exploded	x	x

No.	Substance mixed with Mg	Equivalent weight of Mg (g)	Specific gravity (g/cc)	Hazard Properties		
				by heat	by impact	Ash with water
25	P_2O_5	0.857	—	exploded	x	—
26	$Ca_3(PO_4)_2$	0.862	1.49	x	x	x
27	$Ca(H_2PO_4)_2$	0.868	—	x	x	—
28	$BaCrO_4$	0.384	2.27	x	x	x
29	$K_2Cr_2O_7$	0.579	—	x	x	—
30	$Na_2B_4O_710H_2O$	1.084	—	x	x	—
31	SiO_2	1.619	1.01	x	x	ignited
32	Glass powder	(1.000)	1.61	x	x	—
33	$Na_2(SiF_6)$	0.647	1.68	x	x	x
34	$Mg_3(Si_4O_{10})\bullet(OH)_2$	1.089	1.82	x	x	—
35	BaO_2	0.287	—	x	sparked	ignited
36	MnO_2	0.560	—	x	x	—
37	Fe_2O_3	0.453	2.22	x	x	x
38	Fe_3O_4	0.420	—	x	x	x
39	Cu_2O	0.170	—	x	x	—
40	CuO	0.305	—	x	x	—
41	ZnO	0.299	—	x	x	—
42	Pb_3O_4	0.142	—	x	x	—
43	NaCl	0.201	—	x	x	—
44	KCl	0.159	—	x	x	—
45	C_2Cl_6	0.308	1.71	x	exploded	x
46	$(CF_2)_n$ (Teflon)	0.486	—	x	exploded	x
47	SrF_2	0.193	—	x	x	—
48	Sb_2S_3	0.215	—	x	x	—
49	S	0.660	—	x	x	—
50	Clay	(1.000)	1.65	x	x	x

Notes:

1. Symbols: — : not tested,
   x : the detonation, explosion or ignition were not observed at the heating test, impact test or during the cleaning of the mortar with a wet cloth.
2. The specific gravities were obtained from the samples of flare for the burning test.

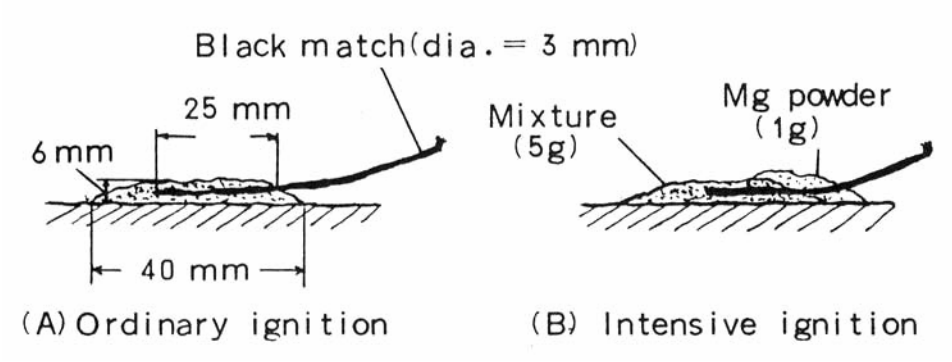

Figure 1. Burning test on the ground.

Burning Test on the Ground

Five grams of each mixture in Table 1 in powder form were placed on a concrete floor in the shape of a sand pile. A black match was inserted into the mixture. It was ignited at the end and the ignition and burning conditions of the mixture were observed. When the ignition was unsuccessful with the black match, a small quantity of Mg powder, about 1 gram, was added and the test was repeated (Figure l). In the blank test No. 1 with only the Mg powder, it firstly burns violently only on the surface of the pile by the help of the air in a short time, and secondly it keeps red-hot condition of 800–900 °C for about 5 minutes being covered with light ash of MgO. This effect is useful for igniting ignition resistant mixtures.

When the mixtures were ignited, they burned generally producing an intensive flame with a sizzle, but some of them without sizzle as the carbonate mixtures, No. 6 or 10, oxalate mixtures, No. 12 or 13 or oxide mixtures, No. 39 or 40, etc. (The chloride mixtures, No. 43 and 44 produced no flame during burning.) After the flame went out, a cinder remained keeping a red-hot state for fairly a long time. It might be caused by a second reaction in the cinder, for example, $Si + 2\ Mg \rightarrow Mg_2Si$. At last a large quantity of ash remained, which was generally black colored due to the reduced carbon or metal.

Heating Test in a Glass Test Tube

About 0.5 grams of each mixture were placed in a glass test tube of 12 mm inside diameter, 150 mm long and a Pt–Rh thermocouple was inserted in it. The tube was heated by an alcohol lamp gently from the bottom, and the conditions of the sample were observed measuring the temperatures. The ignition temperature was obtained when the sample ignited or exploded. The ears had to be covered with cotton, because the explosion noise was often very loud, especially with the mixtures No. 16, 17, 18, 22, 24, 25 and 36. The thermocouple was destroyed almost every test and had to be repaired each time (Figure 2).

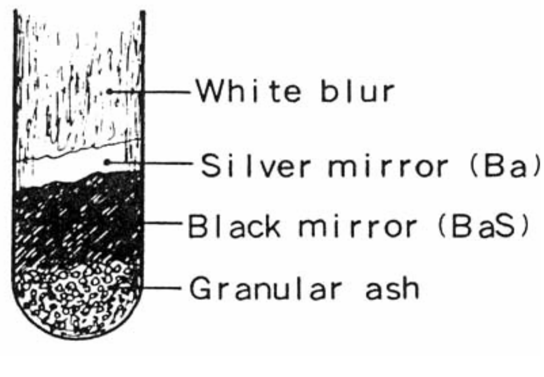

Figure 2. An example of the outside view of test tube after the heating test ($BaSO_4$).

Burning Test as a Flare

Mixtures which were thought to be useful or safe were selected. Eighty grams of each mixture were consolidated without binder by pressing into a paper tube of 33.5 mm inside diameter, 50 mm long and a wall thickness of 1 mm. This flare was placed on a support plate so that the ignition surface came upwards. A piece of black match was placed on the surface and a small quantity, about 1 g, of Mg powder, was sprinkled over it. The match was ignited and the fire proceeded to the Mg powder and then to the flare. When not ignited, it was repeated by blowing. At last, some mixtures were not ignited (No. 3, 7, 17, 26, 28, 33, 34, 37, 41, 50). The flares burned producing a flame of high light intensity and a bulky ash (Figure 6).

With the mixture, H_2O + Mg (No. 2), following compositions were used:

I. 50% Mg + 43% H_2O + 3% $K_2Cr_2O_7$ + 4% starch,
II. 48% Mg + 36% H_2O + 5% $K_2Cr_2O_7$ + 7% $Na_2(SiF_6)$ + 4% starch.

In this case, 100 grams of the gelatinized mixture were loaded in a paper tube of 35 mm inside diameter and wall thickness of 0.5 mm.

The samples, once ignited, continued burning normally except No. 11, sodium oxalate mixture, which burned oscillating with a rather long cycle as it is shown in Figure 3 and producing a bellow-like ash.

Firing Test with a Small Iron Mortar

The same mixtures as used for the flare test were examined. Four grams of each mixture were loaded in a small iron mortar and it was fired with an angle of 45° (Figure 4). The volume of the propellant chamber was 10 cc and the total inside volume of the barrel including the propellant chamber was 200 cc. The projectile was made of a plastic resin and weighed 100 grams. A piece of black match was inserted into the bottom of the barrel through a small hole for ignition. When the propellant was ignited, the bottom block moved down to the stopper by the action of the gas pressure closing the hole. To enlarge the ignition effect, about 0.5 grams of Mg powder were placed in the bottom of the propellant chamber and the propellant grains were charged on it.

For each mixture the firing was carried out two times and the flight distance of the projectile was measured. After the firing the mortar was hot and it was hardly seized by unarmed hand. When the mortar was cooled, it was swept by a wet cloth. The cloth was often ignited during the operation. It might be due to the contact of the water with a reduced metal such as Na, K, Ca or Sr, etc.

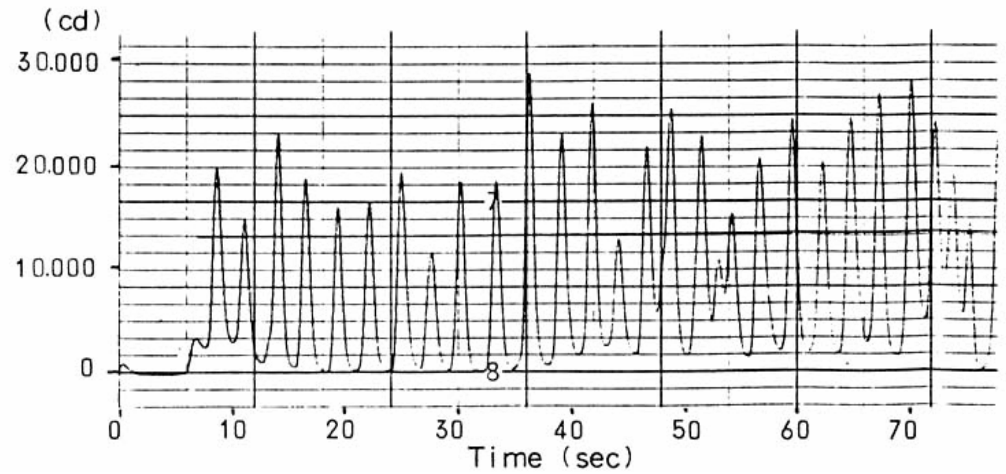

Figure 3. From the burning test of a flare of $Na_2C_2O_4$.

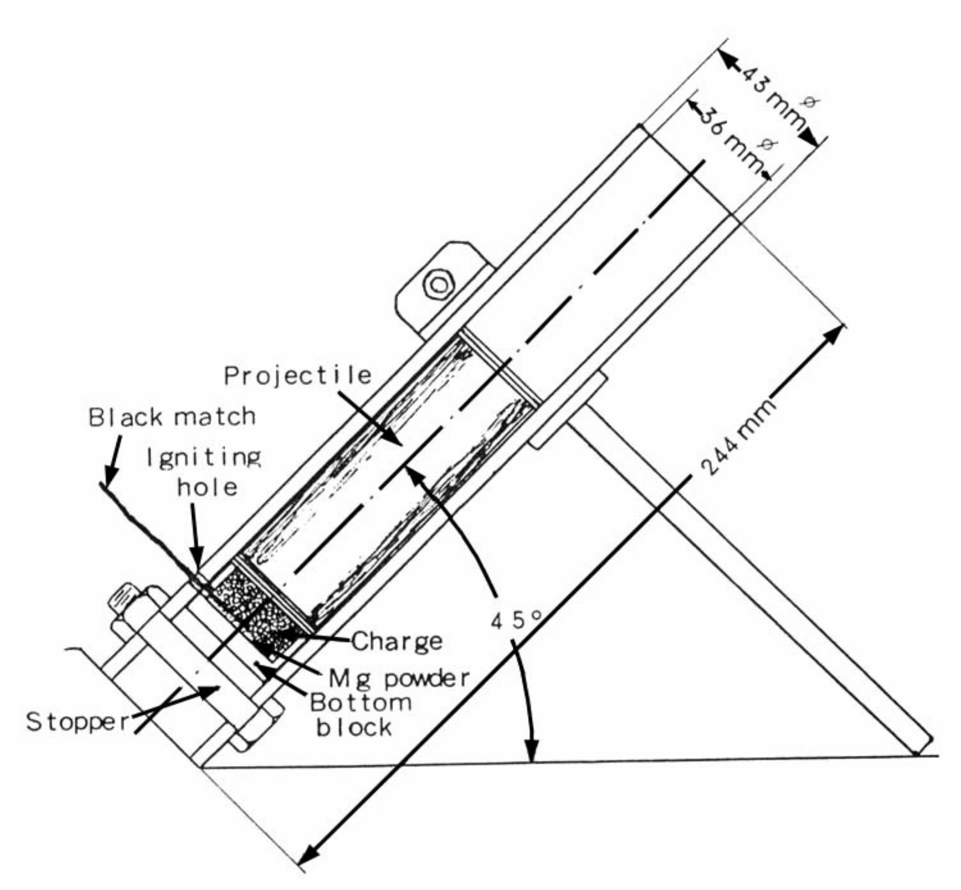

Figure 4. The iron mortar for firing test.

For comparison, the same projectile was fired by using 0.1–0.6 grams of Black Powder as propellant.

Impact Test by an Iron Hammer

To see the hazardous properties of the mixtures, a simple impact test was carried out. About 0.5 grams of each sample were placed on an iron anvil and it was hit with a 3.5 kg iron hammer by hand from a height of about 60 cm. Unexpected explosions occurred with mixtures, No. 15, K_2SO_4; No. 19, $BaSO_4$; No. 45, C_2Cl_6; No. 46, $(CF_2)_n$. Moreover, a slight ignition was observed with No. 16, $MgSO_4$; No. 21, $FeSO_4 \bullet 7H_2O$; No. 35, BaO_2.

Tests for Positive Mixtures for Comparison

With ordinary oxygen donor, $KClO_3$, $KClO_4$, NH_4ClO_4, KNO_3, and $NaNO_3$, which have been used for positive explosives, were examined in combination with Mg by the same test as above.

In determining the ratio of the Mg to the nitrates the following type formula was used:

$$2\,KNO_3 + 9\,Mg \rightarrow 2\,K + Mg_3N_2 + 6\,MgO.$$

Results and Discussions

Table 1 shows a list of negative mixtures which were easily available for the tests. On the list some sulfates or oxides which have been practically used as an oxygen donor may be found. The hazard properties show the negative explosives are not always safe in handling. Especially, a special attention must be paid to the

Table 2. A List of Positive Mixtures for Comparison.

No.	Substance mixed with Mg	Equivalent weight of Mg (g)	Specific gravity (g/cc)	Hazard properties by heat	Hazard properties by impact	Hazard properties Ash with water
51	$KClO_3$	0.794	—	x	exploded	—
52	$KClO_4$	0.819	1.79	x	exploded	x
53	NH_4ClO_4	1.035	—	x	exploded	—
54	KNO_3	1.082	1.63	x	exploded	x
55	$NaNO_3$	1.287	1.67	detonated	exploded	ignited

Note:

1. Symbols: — : not tested,
   x : the detonation, explosion or ignition were not observed at the heating test, impact test or during the cleaning of the mortar with a wet cloth.
2. The specific gravities were obtained from the samples of flare for the burning test.

detonation or explosion properties of some sulfates on heating, because there may be a risk that the burning changes to the detonation. One of the positive mixtures in Table 2, $NaNO_3$ (No. 55), might have the same tendency as above. However, when the mixtures are consolidated, the tendency might be different from the results. Many types of ash from the negative mixtures after the burning in a closed vessel ignite and burn with water. This is a special effect with these mixtures. The P_2O_5 mixture (No. 25) ignites producing a large flash when a drop of water was added to it. This effect might be useful for an ignition device in presence of water. Comparing with the results of positive mixtures in Table 2, it could be said the hazard properties of the negative are generally lower than those of the positive.

The ignition tendencies of mixtures including those of the positive mixtures in Table 2 are classified into eight ranks from the results of the burning test on the ground by black match. They are shown in Figure 5 in combination with the ignition temperatures from the results of the heating test in a glass test tube. The figures attached to each mark denote the number of the mixture. It is rather difficult to find the relation between the classes and ignition temperatures which are brought from different tests. With a bird's-eye view, however, the lower the ignition temperatures, the lower the ranks. Class 1 and 2 are occupied by the positive mixtures, because they are very easily ignited.

It is also difficult to find the relation between the ignition tendencies and the burning properties in Figure 5 in which the shape of each symbol denotes the burning condition of the mixture. Fifteen mixtures which belong to Class 3 showed a good ignition and a good burning property, especially with the mixtures, No. 14 (Na_2SO_4), No. 21 ($FeSO_4•7H_2O$), No. 23 ($NiSO_4•7H_2O$), No. 27 ($ca(H_2PO_4)_2$, No. 29 ($K_2Cr_2O_7$). In general, the mixture of a substance which contains water of crystallization belongs to this class. Four mixtures which belong to Class 7 showed a good burning property in spite of their poor ignition tendency (No. 17 ($CaSO_4•½H_2O$), No. 22 ($CuSO_4$), No. 27 ($MgSO_4$), No. 30 ($Na_2B_4O_7•10H_2O$)). The ignition tendencies are different from the above when the mixtures are consolidated as it was in the flare test, where the mixtures, No. 7 ($CaCO_3$), No. 26 ($Ca_3(PO_4)_2$), No. 28 ($BaCrO_4$), No. 33 ($Na_2(SiF_6)$, No. 37 (Fe_2O_3), No. 41 (ZnO), No. 50 (clay), could not be ignited even when using Mg powder with the black match as the igniter.

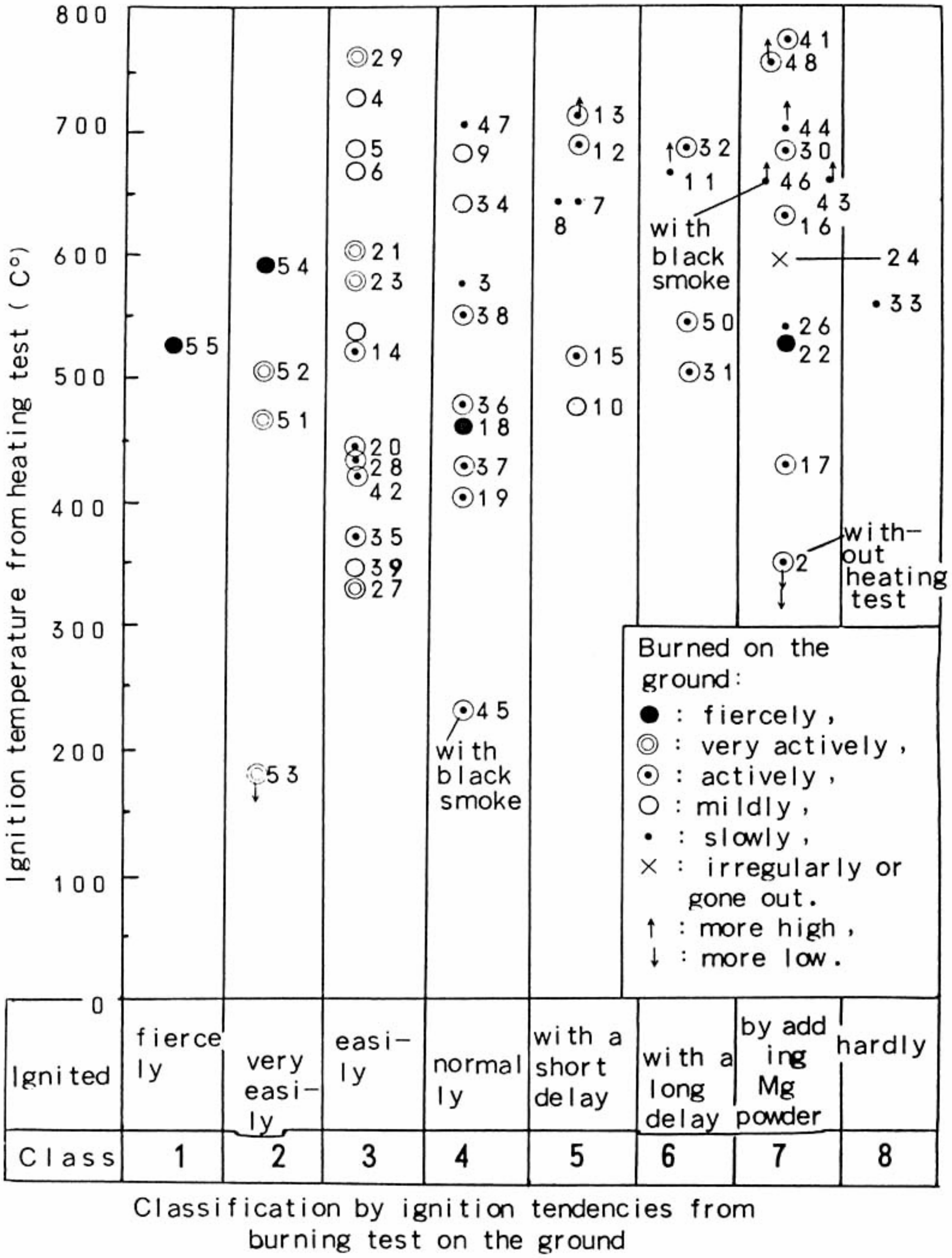

Figure 5. Ignition tendencies, ignition temperatures and burning conditions of mixtures.

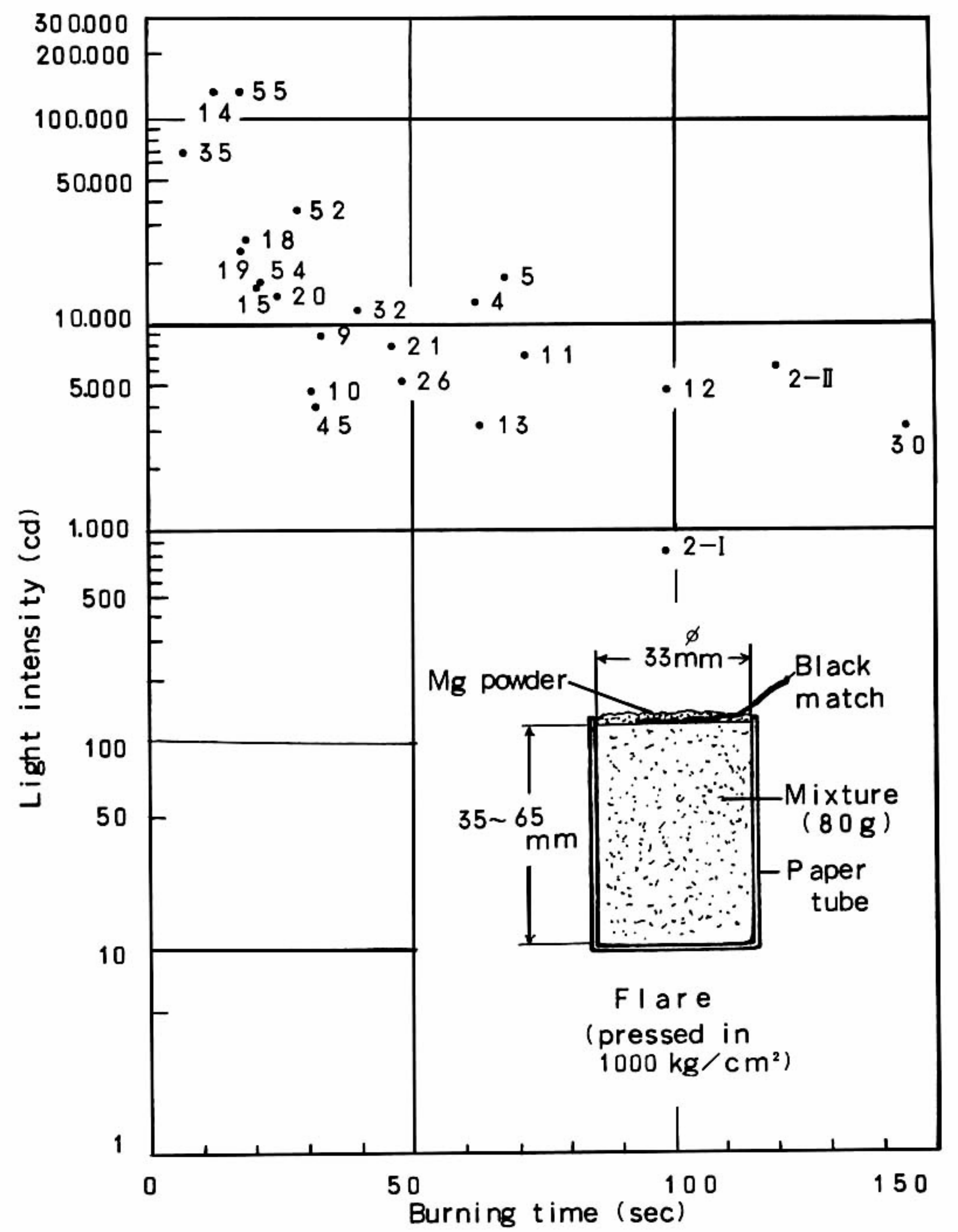

Figure 6. The results of the burning test of flares.

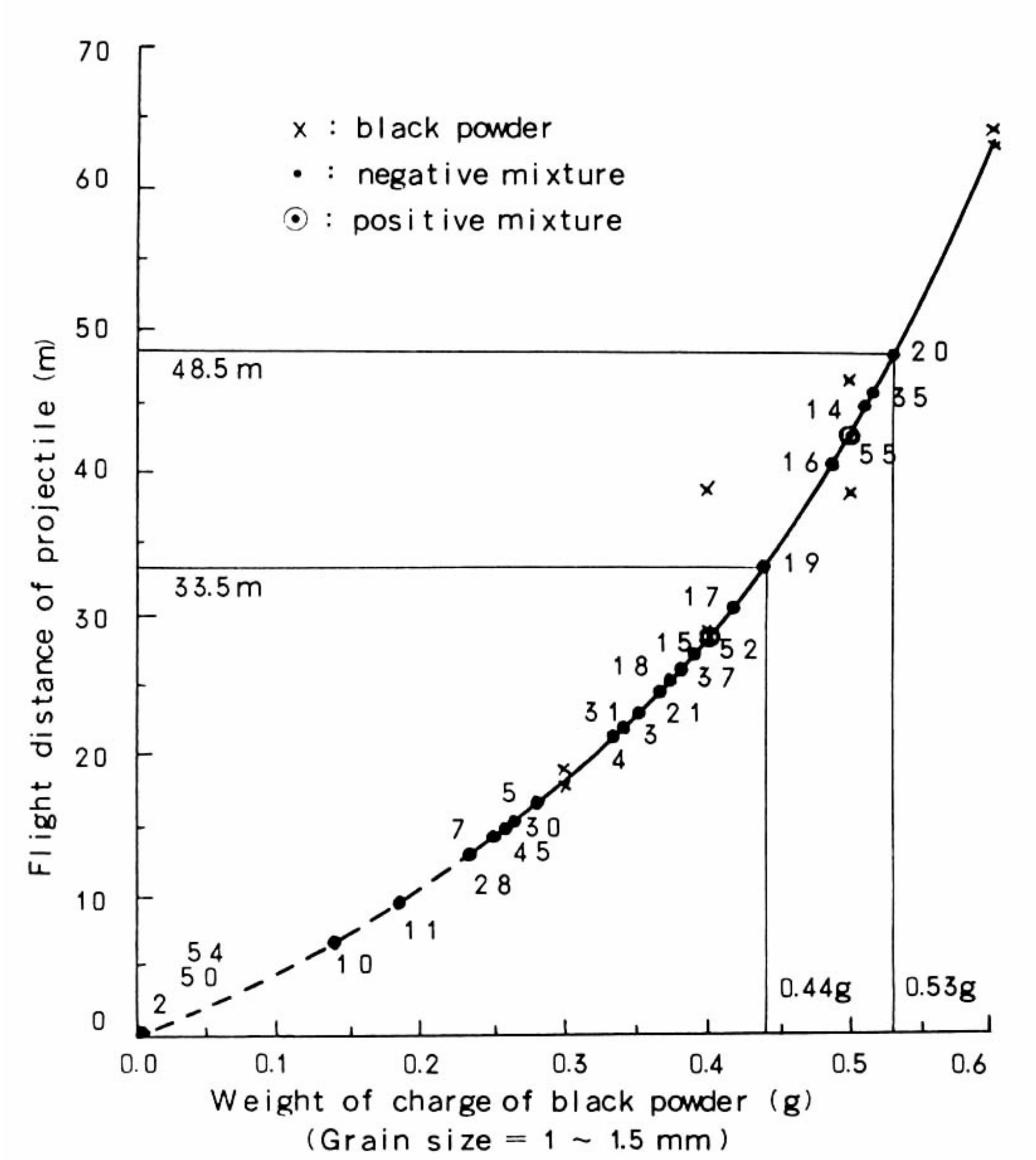

Figure 7. The results of the firing test comparing with those of Black Powder charges.

The relations between the light intensity and the burning time are shown in Figure 6 from the results of the burning test of the mixtures as a flare. The mixture No. 14 (Na_2SO_4) shows a very high light intensity and the effect is almost the same as that of No. 55 ($NaNO_3$) which belongs to the positive mixture. The mixtures which can be used in place of the ordinary positive illuminants may be No. 18 ($SrSO_4$), No. 19 ($BaSO_4$), No. 5 ($NaHCO_3$) or No. 4 (Na_2CO_3), etc. No. 2-II (H_2O) may be also useful for a long time illumination.

The curve in the Figure 7 shows the relation between the weight of charge of Black Powder, which has been popularly used for lifting firework shells, and the flight distance of the projectile. From the curve we can see the flight distance of the projectile by a 4 gram charge of a mixture and the quantity of the Black Powder which gives the same ballistic effect as the 4 gram charge. The black round marks in the curve show the relation with the negative mixtures and the white the positive ones. For example, the flight distance by a 4 gram charge with No. 20 ($A1_2(SO_4)_3 \cdot 18H_2O$) is 48.5 meters and the corresponding quantity of the Black Powder is 0.53 grams and with No. 19 ($BaSO_4$) 33.5 meters and 0.44 grams. In general, the ballistic effect of the negative mixtures may be estimated 1/10 as large as that of the Black Powder. The effects of the positive mixtures are not always larger than those of the negative ones.

In general, negative mixtures leave red-hot cinder for several minutes after they burn up except with sulfates or oxide mixtures. This effect may be useful for some devices. The mixtures, 2–I or 2–II are also an exception. They burn producing a light bulky ash of MgO. The positive mixtures leave almost no cinder after burning.

A Proposal for the Use of the Negative Mixtures

1) The low ballistic force may be used for some devices such as actuators or instruments for house blasting in the city, where too powerful explosives cannot be used.
2) The red-hot cinder may be used for some igniters or temporal heaters.
3) The mixture of chloride, NaCl or KCl, may be used for a long time delay.
4) The mixture of P_2O_5 may be used for some ignition devices in presence of water.
5) The mixture of SiO_2 or glass powder may be used for some fireworks to display a special effect by the spontaneous ignition of Mg_2Si when it is added with acid solution.
6) The mixtures of sodium salts are always useful to obtain a high light intensity as a flare.
7) The mixture of H_2O or earth (clay) may be used for a cheapest illuminant.

When the negative explosives are practically used, a perfect damp-proofing and some appropriate measures to avoid the reaction between Mg and the other substance are necessary.

Conclusion

The negative explosive has been defined as a mixture of some metal powder which has a large reduction capacity and a substance which contains O, Cl or F, etc. and which was not used as the conventional oxidizer for ordinary explosives.

The characteristics of the negative explosives were examined with about 50 mixtures which consisted of a Mg powder and a substance by burning on the ground, heating in a glass test tube, burning as an illuminant, firing as a propellant and blowing by 2.5 kg hammer. For comparison, 5 mixtures which consisted of the Mg powder and a conventional oxidizer were examined as positive explosives.

The results were discussed on hazard properties, ignition temperatures and ignition tendencies, illuminant effects, propellant effects and cinder formations.

A proposal for the use of the negative explosives has been made.

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Ballistics of Firework Shells

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ABSTRACT

Heretofore we have had four important problems with calculations in this field, i.e., with the interior ballistics when using Black Powder as the propellant:

(1) to obtain a suitable form function of the propellant which consists of irregular grains,

(2) to obtain solutions when the burning rate of the propellant grains is proportional to P^α, where P is an internal pressure of the mortar barrel and α the pressure exponent,

(3) to obtain suitable solutions when the propellant gas escapes from the burning room through the clearance between the wall and the shell in the mortar, and with the exterior ballistics

(4) to obtain simply the drag coefficient for various shapes of shells.

For (1) a treatment to calculate the surface areas and volumes of grains assuming the propellant grains consist of a mixture of cubes and spheres is proposed. For (2) a method to solve a three order differential equation derived from three basic interior ballistic equations step by step with proper time intervals is proposed. For (3) the nozzle theory used for rocket engines is introduced. For (4) the fact that the maximum height of the projectile in the air is almost the same as that of vacuum when the flying times of the both are equal is applied.

These methods are applied to 6-inch shells and examined if they are suitable in practice.

Introduction

We cannot lift firework shells without the oldest Black Powder even today, because smokeless powder only burns in the mortar leaving the shell at the bottom unmoved. However, the development of theoretical treatment of the interior ballistics using Black Powder in this has been too slow. I tried in the past to solve this problem,[1] but it was only a shift because I used the method which had been used for smokeless powder to cannons.

The differences between the ballistic characters of black and smokeless powders may be in three points: a large burning rate of the former at the atmospheric pressure which is about ten times as large as that of smokeless powder, a low force of explosives of the former of about one third of the latter and a low pressure exponent value of about 0.5 which is about one half of the latter. I proposed here a step by step method to solve the ballistic equations with these points. In this process, the difference between the firework mortar and the cannon is also considered: the former has a rather large clearance between the wall and shell in the barrel which may cause an unnegligible gas flow out.

In the next, I proposed a method of exterior ballistics to find the drag coefficient of the shell having data of the muzzle velocity and the time of flight from the start to the fall on to the ground. This method may be sometimes useful.

Symbols for Interior Ballistics

A	"Vivacity" of propellant: the burning ratio dz/dt at one atmosphere
Ae	Clearance area between the wall and the shell in the barrel
C	Volume of the barrel
c	Volume of the barrel behind the shell at the time t
c_0	Initial volume of the barrel behind the shell at the time t = 0
d_b	Diameter of the barrel
d_s	Diameter of the shell
f	Force of explosives (Impetus)
g	Gravitational acceleration
i	Ballistic coefficient or denotes the end of the i th time interval
K	Adiabatic expansion constant
k	Ratio of the sectional area of the shell to that of the barrel
n	Average adiabatic expansion coefficient from 0 K to the gas temperature T K
P	Pressure in the barrel
P_0	Atmospheric pressure
V	Muzzle velocity of the shell
v	Velocity of the shell in the barrel
W	Weight of the shell
z	Burning ratio: ratio of the burnt mass to the initial mass of the propellant charge
x	Moving distance of the shell from the origin in the barrel
t	Time of movement of the shell
Δt	Small time interval for calculation
α	Pressure exponent coefficient
γ	Adiabatic expansion coefficient
δ	Density of the Black Powder grains
η	Co-volume
η_z	Practical co-volume
θ	Angle of inclination of the mortar from the horizontal
λ	Coefficient of the propellant mass in imaginary mass of the shell
μ	Imaginary mass of the shell including the propellant mass
Σ	Sum of values
σ	Sectional area of the barrel
$\varphi(z)$	Form function of the propellant grains
Ψ	Flow out coefficient of the gas
ω	Weight of the charge
$\dot{\omega}$	Weight of the flow out gas per second

Superscripts:
One dot (example: x'): Derivative with respect to time
Two dots (example: x''): Second derivative with respect to time
Three dots (example: x'''): Third derivative with respect to time

Subscripts or superscripts:
i End of the i-th time interval on calculation
i–1 Beginning of the i–1-th time interval on calculation

Form Function of Black Powder Grains

The theoretical form function of a propellant grain is generally expressed as $\varphi(z) = S/S_0$ as a function of z, where S is the surface area of a grain at a burning ratio z and S_0 that of the initial at $z = 0$. However, the grains of Black Powder are very irregular in shape and size and the ordinary method of calculation is not useful (Figure1).

A hypothesis is proposed that the powder is a mixture of cubic grains and spherical grains and the side length of the former is the same as the diameter of the latter (Figure 2).

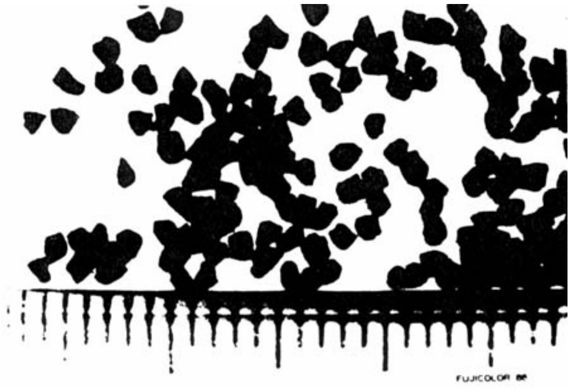

Figure 1. Configurations of Black Powder grains between two sieve openings 0.850 mm and 1.000 mm. The scale is in mm. (Table 1. No. 8)

The burning times of the cube and sphere are the same at the same pressure, but the burning surface area of the former is about two times as large as that of the latter. Therefore, by mixing both of the grains in a proper ratio we have a hypothetical Black Powder which makes us easy to calculate the form function which could resemble that of the real Black Powder.

The real Black Powder is firstly divided into some ranks of size using sieves. The calculation for mixing the cubes and spheres is carried out as follows. For each group of size

$$n_c + n_s = N \tag{1}$$

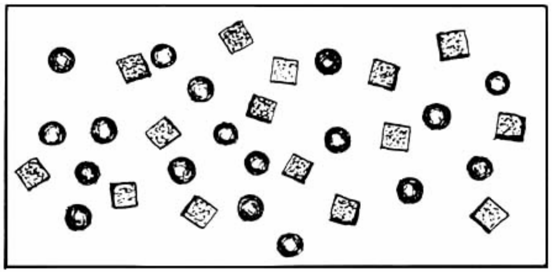

Figure 2. Hypothetical Black Powder grains which consist of cubes and spheres.

$$n_c w_c + n_s w_s = W_g \tag{2}$$

where

N is the total number of the grains in the real powder,

n_c the number of cubes,

n_s the number of spheres,

W_g the total weight of the grains in the real powder,

w_c the weight of a cube,

w_s the weight of a sphere.

Solving these equations we have

$$n_s = \frac{N w_c - W_g}{w_c - w_s} \tag{3}$$

$$n_c = N - n_s \tag{4}$$

Table 1. Data of Grains of 1 kg Black Powder.

No.	Opening of sieve (mm)	Average size of a grain (mm)	Total weight of grains W_g (kg)	Number of grains N	Number of spheres n_s
1	0.175–0.210	0.193	0.000540	65,060	46,380
2	0.210–0.355	0.283	0.017555	452,448	20,687
3	0.355–0.425	0.390	0.089903	1,228,183	760,356
4	0.425–0.500	0.463	0.099759	813,032	501,033
S	0.500–0.600	0.550	0.190329	895,666	507,981
6	0.600–0.710	0.655	0.207554	666,519	513,002
7	0.710–0.850	0.780	0.196098	321,630	179,468
8	0.850–1.000	0.925	0.164907	177,186	122,006
9	1.000–1.180	1.090	0.030836	21,048	15,620
10	1.180–1.400	1.290	0.001444	651	560

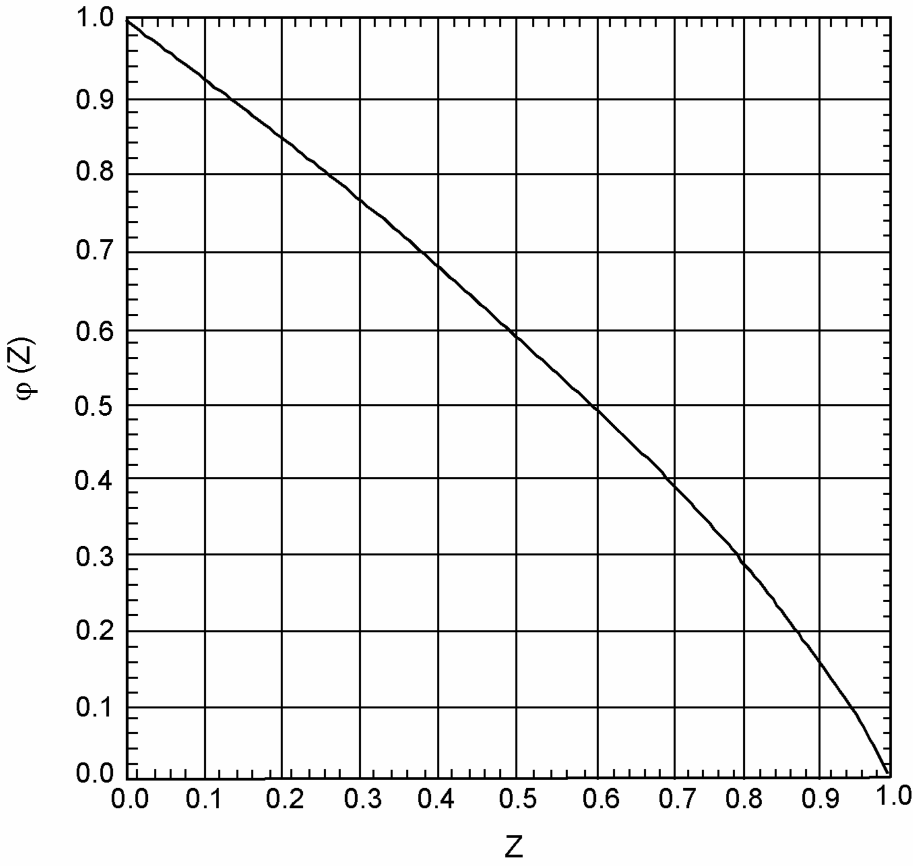

Figure 3. Form function of Black Powder grains due to a hypothetical mixture of cubes and spheres.

Example

Propellant: "Small Grain Black Powder" manufactured by Nippon Kayaku Co., which is most popularly used for lifting charge of firework shells in Japan.

The grains were ranked into 10 groups by sieving l00 grams of the powder using 11 sieves.

In Table 1 the average size of a grain was obtained by averaging the upper and lower openings of the sieves. When sieving, there was a small loss of powder, 1.3 grams, and the values of W_g were magnified proportionately with each obtained weight. A powdered part 0.001075 kg that passed the sieve of 0.175 mm is omitted. For each group the number of grains was practically counted with 1000 to 3000 and the total weight was measured. From these data the values of N were determined.

For the hypothetical mixture the weight of a grain was calculated by following formulas:

for the cube $w_c = 1.75 \times \ell^3$,

for the sphere $w_s = 1.75 \times 4/3\ \pi\ r^3$

where the value 1.75 is the density of the real Black Powder (g/cc), ℓ the side length of the cube, r the radius of the sphere where $2r=\ell$.

The burning velocity of the Black Powder was measured by burning three compressed blocks (density: 1.75 g/cm^3) of the sample powder in the open air and an average value of 9.52 mm/s was obtained. In the atmospheric pressure the grains will burn from their surface to each centre with this rate. The volume and the burning surface area were calculated with the time for each group. Multiplying these data by the number of grains n_c or n_s and summing these data with the time with each group and then with all groups, the sum of the volumes and the burning areas with all grains were ob-

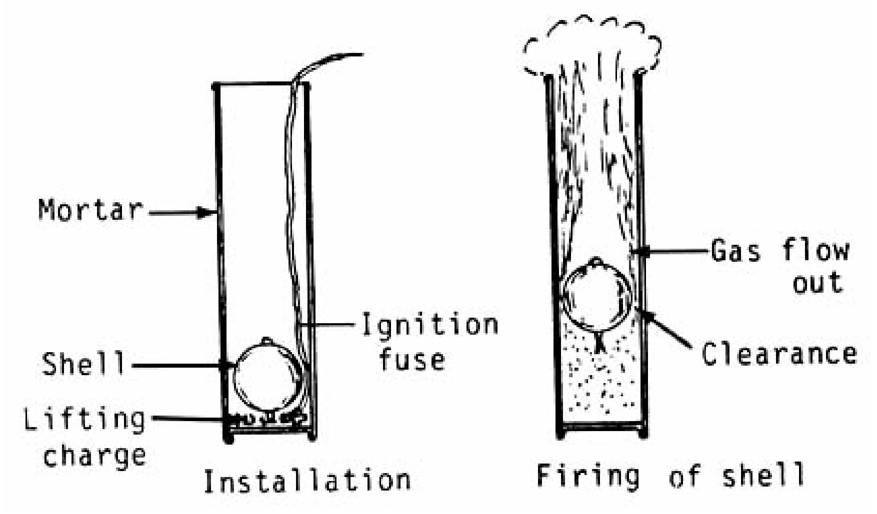

Figure 4. Loading and firing of shell.

tained as functions of time. The burning ratio z and the form function φ(z) were calculated by the following formulas:

$z = 1 - V/V_0$ for time t, (4)

$\varphi(z) = S/S_0$ for time t, (5)

where V is the sum of volumes, V_0 the initial value of V, S the sum of the burning surface areas, S_0 the initial value of S. In combination of (4) and (5) a curve of $z - \varphi(z)$ was obtained as it is shown in Figure 3.

Vivacity of Black Powder

Vivacity is a characteristic value which generally represents the burning ratio at one atmospheric pressure when the grains begin to burn. Using the data obtained by the studies of the form function, the value was determined as follows: [3]

$$\begin{aligned} A &= S_0\, w\, \delta \qquad (6)\\ &= 559.83 \times 0.0952 \times 1.75\\ &= 93.27\ \mathrm{s}^{-1} \end{aligned}$$

where $S_0 = 559.83\ \mathrm{dm}^2$, w is the burning rate = 0.0952 dm/s, $\delta = 1.75\ \mathrm{kg/dm}^3$.

Interior Ballistic Solution

The mortar is usually installed vertically on the ground as it is seen in Figure 4. In the installation the clearance around the shell is important to ignite the lifting charge from upside. When ignited, the gas and smoke firstly appears from the muzzle and then the shell.

The energy conservation is expressed as

$$\frac{f\left(\omega z-\int \dot{\omega}\, dt\right)}{n-1}=\frac{1}{2}\mu v^{2}+\frac{\left(P-P_{0}\right)\left(c-\eta_{z}\omega\right)}{n-1} \qquad (7)$$

where

$$\eta_{z}=\frac{1}{\delta}+\left(\eta-\frac{1}{\delta}\right)z \qquad (8)$$

The equation of motion of shell is

$$\mu\frac{dv}{dt}=k\sigma\left(P-P_{0}\right)-W\sin\theta$$

$$\mu=i\frac{W}{g}\left(1-\lambda\frac{\omega}{W}\right) \qquad (9)$$

Generally, the mortar is installed vertically on the ground and sinθ =1.

The burning of Black Powder is defined[2] as

$$\frac{\mathrm{d}z}{\mathrm{d}t} = A\varphi(z)\left(P/P_0\right)^{\alpha}, \quad \text{where } \alpha = 1/2 . \tag{10}$$

The gas flow out is expressed as[4]

$$\dot{\omega} = Ae\, P\Psi \,/\, f^{\frac{1}{2}}$$

$$\Psi = \left(\frac{2}{\gamma+1}\right)^{\frac{1}{\gamma-1}} \left\{2g\left(\frac{\gamma}{\gamma+1}\right)\right\}^{\frac{1}{2}} \tag{11}$$

under the condition

$$P_0 / P < \left\{2/(\gamma+1)\right\}^{\{\gamma/(\gamma-1)\}} \tag{12}$$

After the lifting charge has burnt out

$$P(c-\eta)^{\gamma} = K \tag{13}$$

By differentiating equation (7) with respect to t, we have

$$\begin{aligned} f\left(\omega\frac{dz}{dt} - \dot{\omega}\right) &= (n-1)\ \mu x' \cdot x'' \\ &+ \frac{dP}{dt}\left[\sigma x + c_0 - \left\{\frac{1}{\delta} + \left(\eta - \frac{1}{\delta}\right)z\right\}\omega\right] \\ &+ (P - P_0)\left\{\sigma x'' - \left(\eta - \frac{1}{\delta}\right)\omega\frac{dz}{dt}\right\} \end{aligned} \tag{14}$$

By differentiating equation (9)

$$\frac{dP}{dt} = \frac{\mu}{k\sigma}x''' \tag{15}$$

By substituting equation (15) for dP/dt in equation (14) we have equation 16:

From equation (9) the pressure is found:

$$P = \frac{\mu}{k\sigma}x'' + \frac{W}{k\sigma} + P_0 \tag{17}$$

The sum of the gas flow out could be expressed as

$$\int \dot{\omega}\ dt = \sum{}^{i}\ \frac{1}{2}\left(\dot{\omega}_{i-1} + \dot{\omega}_i\right)\ \Delta t \tag{18}$$

From equation (7) the burning ratio is found:

$$z = \frac{\int \dot{\omega}\ dt\ +\ \frac{n\text{-}1}{2}\mu x'^2 + (P - P_0)\left(\sigma x +\ c_0 - \frac{\omega}{\delta}\right)}{\omega\left\{f + \left(\eta - \frac{1}{\delta}\right)(P - P_0)\right\}} \tag{19}$$

It is possible to solve equation (16) in combination with equations (10), (11), (17), (18) and (19) by a step and step method. The calculation program was planned as it is shown in Table 2.

Table 2. A Program to Solve Interior Ballistic Equations for the Shell.

(1)	x'''_{i-1}
(2)	x''_{i-1}
(3)	x'_{i-1}
(4)	x_{i-1}
(5)	x'''_{i}
(6)	$\Delta x'' = ½ \{(1) + (5)\} \Delta t$
(7)	$x''_i = (6) + (2)$
(8)	$\Delta x' = ½ \{(7) + (2)\} \Delta t$
(9)	$x'_i = (8) + (3)$
(10)	$\Delta x = ½ \{(9) + (3)\}\Delta t$
(11)	$x_i = (10) + (4)$

$$x''' = \frac{k}{\mu}\,\frac{f\left(\omega\frac{dz}{dt} - \dot{\omega}\right) - (n-1)\ \mu x' x'' - \sigma\ (P - P_0)\left\{x' - \left(\eta - \frac{1}{\delta}\right)\frac{\omega}{\sigma}\frac{dz}{dt}\right\}}{x + \frac{c_0}{\sigma} - \left\{\frac{1}{\delta} + \left(\eta - \frac{1}{\delta}\right)z\right\}\frac{\omega}{\sigma}} \tag{16}$$

(12)	$\frac{\mu}{k\sigma}\times\ (7)$
(13)	$(12) + W / k\sigma + P_0 = P_i$
(14)	$P_i - P_0 = (13) - P_0$
(15)	$\dot{\omega}_{i-1}$
(16)	$\sum^{i-1}\dot{\omega}\ \Delta t$
(17)	$P_0\ / P_i$
(18)	$\dot{\omega}_i = \left(Ae\ \Psi / f^{\frac{1}{2}}\right)\times\ (13)$
(19)	$\sum^{i}\dot{\omega}\ \Delta t = (16) + \frac{1}{2}\left\{(15)+(18)\right\}\Delta t$
(20)	$f\times\sum^{i}\dot{\omega}\Delta t = f\times(19)$
(21)	$\frac{n-1}{2}\mu v^2 = \frac{n-1}{2}\mu\times(9)^2$
(22)	$\sigma x = \sigma\times(11)$
(23)	$c = c_0 + \sigma x = c_0 + (22)$
(24)	$c - \frac{\omega}{\delta}$
(25)	$(P_i - P_0)\left(c - \frac{\omega}{\delta}\right) = (14)\times(24)$
(26)	$(20) + (21) + (25)$
(27)	$\left(\eta-\frac{1}{\delta}\right)\left(P_i - P_0\right) = \left(\eta-\frac{1}{\delta}\right)\times(14)$
(28)	$(27) + f$
(29)	$\omega\times(28)$
(30)	$z = (26) / (29)$
(31)	$\varphi(z)$: from Figure
(32)	$\left(\frac{P_i}{P_0}\right)^{\alpha} = \left(\frac{(13)}{P_0}\right)^{\frac{1}{2}}$
(33)	$\frac{\mathrm{d}z}{\mathrm{d}t} = A\ \varphi(z)\times\left(\frac{P_i}{P_0}\right)^{\frac{1}{2}}$ $= A\times(31)\times(32)$
(34)	$\omega_{\mathrm{i}}\frac{\mathrm{d}z}{\mathrm{d}t} = \omega_{\mathrm{i}}\times\ (33)$

(35)	$\omega_{\mathrm{i}}\frac{\mathrm{d}z}{\mathrm{d}t} - \omega_{\mathrm{i}} =\ (34) - (18)$
(36)	$f\left(\omega_i\frac{\mathrm{d}z}{\mathrm{d}t} - \dot{\omega}\right) = f\times(35)$
(37)	$(n-1)\mu\cdot x'\cdot x'' = (n-1)\times(9)\times(7)$
(38)	$\left(\eta-\frac{1}{\delta}\right)\frac{\omega}{\sigma}\frac{\mathrm{d}z}{\mathrm{d}t} = \left(\eta-\frac{1}{\delta}\right)\frac{\omega}{\sigma}\times(33)$
(39)	$x - \left(\eta-\frac{1}{\delta}\right)\frac{\omega}{\sigma}\frac{\mathrm{d}z}{\mathrm{d}t} = (9) - (38)$
(40)	$\sigma\left(P_i - P_0\right)\left\{x' - \left(\eta-\frac{1}{\delta}\right)\frac{\omega}{\sigma}\frac{\mathrm{d}z}{\mathrm{d}t}\right\}$ $= \sigma\times(14)\times(39)$
(41)	$(36) - (37) - (40)$
(42)	$\left(\eta-\frac{1}{\delta}\right)z = \left(\eta-\frac{1}{\delta}\right)\times(30)$
(43)	$\left(\eta-\frac{1}{\delta}\right)\ z\ + \frac{1}{\delta} = (42) + \frac{1}{\delta}$
(44)	$\left\{\left(\eta-\frac{1}{\delta}\right)\ z\ + \frac{1}{\delta}\right\}\frac{\omega}{\sigma} = (43) + \frac{\omega}{\sigma}$
(45)	$x + \frac{c_0}{\sigma} - \left\{\left(\eta-\frac{1}{\delta}\right)\ z\ + \frac{1}{\delta}\right\}\frac{\omega}{\sigma}$ $= (11) + \frac{c_0}{\sigma} - (44)$
(46)	$x''' = \frac{k}{\mu}\times{}^{(41)}\!/_{(45)}$

In the program, the values of (1)–(4), (15), and (16) come from the former interval. Firstly, a value of x_i''' which is expected from the values of the former intervals, is put into (5). However, at the first interval we cannot expect the value. Therefore we use a proper value of x_i''' in this case, for example x_i''' = 500,000,000 dm/s^3.

With a time interval Δt (Example: 0.0001 s) the calculation proceeds from (1) to (46). The value of (46) is introduced again to (1) and the calculation is repeated. On repeated iterations, the value of x_i''' approaches a definite value or the difference of the value from the former becomes allowable. Then we proceeded to the next time interval.

Example

Data: A 6 inch round shell, weight: 1.25 kg, inside length of mortar: 103cm

(1)	f	= 0.2934×10^6 dm·kg/kg[2]
(2)	A	= $93.268\ \text{s}^{-1}$
(3)	$\varphi(z)$	from Figure 5
(4)	ω	= 0.0750 kg
(5)	W	= 1.250 kg
(6)	g	= $98.0\ \text{dm/s}^2$
(7)	i	= 1
(8)	μ	= $i\dfrac{W}{g}\left(1+\lambda\dfrac{\omega}{W}\right)=0.01314\dfrac{\text{kg}\cdot\text{sec}^2}{\text{dm}}$
(9)	σ	= $\pi d_b^2/4 = 1.887\ \text{dm}^2$
(10)	s	= $\pi d_s^2/4 = 1.584\ \text{dm}^2$
(11)	Ae	= $\sigma - s = 0.303\ \text{dm}^2$
(12)	s/σ	= k = 0.8394
(13)	P_0	= $103.33\ \text{kg/dm}^2$
(14)	δ	= $1.75\ \text{kg/dm}^3$
(15)	η	= $0.983\ \text{dm}^3/\text{kg}$
(16)	γ	= 1.214
(17)	n	= 1.260

The results are summarized in Figure 5.

A Method for the Calculation of the Drag Coefficient of a Shell in Air

Having the data of muzzle velocity and flying time from the start to the fall on to the ground, the drag coefficient of the shell is simply calculated. Generally the movement of a projectile in the air is expressed by equations (20) and (21). When the shell is vertically fired on the ground, sinθ = 1, and (21) could be omitted.

$$\frac{W}{g}\frac{\mathrm{d}v}{\mathrm{d}t} = -K\ s\ v^2 - W\ \sin\theta \tag{20}$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = -\frac{g\ \cos\theta}{v} \tag{21}$$

K is defined with the drag coefficient C_D as

$$K = C_D \times \frac{1}{2}\frac{\rho}{g} \tag{22}$$

From (20), formulas (23), (24) and (25) are derived.[5]

$$a = (W/KS)^{½} \tag{23}$$

$$x = V/a \tag{24}$$

$$H = \frac{a^2}{2g} \times 2.303\ \log(x^2+1) \tag{25}$$

Due to the fact that the maximum height is almost the same as that in the vacuum with the same flying time from the start to the fall [6]

$$H_{(Vacuum)} = \frac{1}{8} g\ T^2_{(Air)} = H \tag{26}$$

In the equations

θ	inclination from the horizontal,
K	a constant which includes the drag coefficient C_D,
C_D	the drag coefficient,
ρ	density of air
V	the muzzle velocity of the shell,
a	a parameter,
x	a parameter,
H	the maximum height,
$H_{(Vacuum)}$	the maximum height in the vacuum,
$T_{(Air)}$	the flying time in the air,
S	the sectional area of the shell.

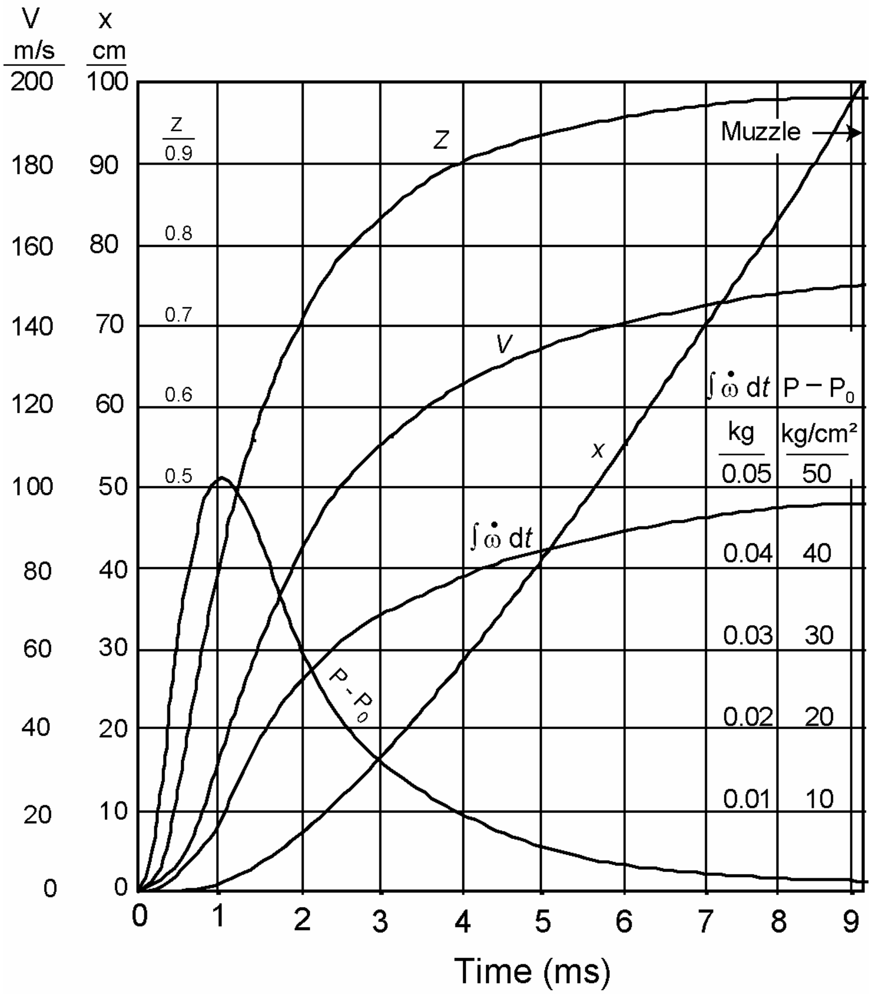

Figure 5. Results of calculation for a 6-inch shell.

When the velocity in the air does not exceed 250 m/s, it could be assumed that the value of C_D is a constant.

By substituting (24) for a in (25) we have

$$\frac{H}{V^2} = 0.1175 \frac{1}{x^2} \log(1+x) \qquad (27)$$

For the equation (27) a diagram is prepared as Figure 6.

Example

Data: A 6-inch round shell,

S	$0.01584\ m^2$
g	$9.80\ m/s^2$
ρ	$l.280\ kg/m^3$
V	$129\ m/s$
$T_{(Air)}$	$14.5\ s$
W	$1.250\ kg$

From (26)

$H = 9.80 \times 14.5^2 / 8 = 258$,

therefore

$H/V^2 = 258/129^2 = 0.0155$.

From Figure 6 $x = 2.55$ is obtained.

From (24)

$a = 129/2.55 = 50.59$.

From (23)

$K = 1.250/(50.59^2 \times 0.01584) = 0.03084$.

From (22)

$C_D = 0.03084 \times 2 \times 9.8 / 1.280 = 0.472$.

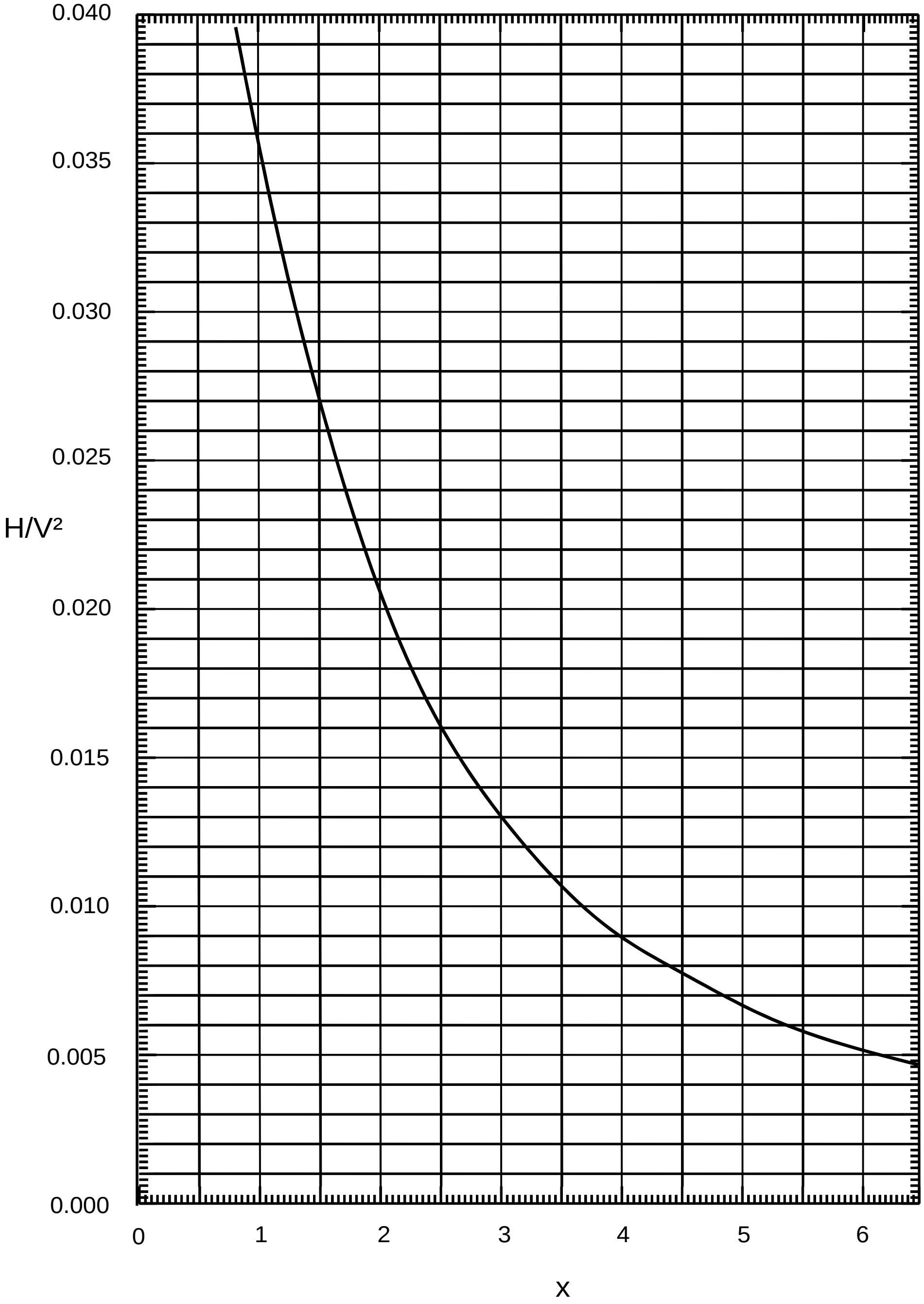

Figure 6. Diagram for equation (27).

Discussion and Conclusion

A method to determine the form function for irregularly shaped Black Powder grains by using a concept of a hypothetical mixture which consists of cubes and spheres is proposed. It may be a way to treat an irregularly shaped material by calculation. There is no way to prove if the mixture exactly resembles the real Black Powder in the surface estimation, but this method seems useful.

A step by step method for solving interior ballistic equations under the condition the pressure exponent $\alpha = 1/2$ is proposed. Comparing the results of calculation for a 6-inch shell with those of my past experiment, it is found that the muzzle velocity from this calculation is 150 m/s when the weight of the shell is 1.25 kg, while those of the experiment were 120 m/s when the weight was 1.25 kg and 152 m/s when the weight was 0.61 kg.[7] Therefore, when we use this method of calculation, the value of the ballistic coefficient should be 2.0 (equation (9))

In the calculation, the gas flow out has been considered, however, the escape of the grains has been ignored. The reason why the value of the ballistic coefficient is so large may be in that in the case of firing, a little quantity of the grains escape out of the barrel without effect. The quantity of the escaped grain is estimated by a calculation for the example as about 4.6 grams.

A method of calculation of the drag coefficient by a simple process having the data of the muzzle velocity and the flying time from the start to the fall on to the ground with shells. The value of the drag coefficient of a 6-inch shell calculated as an example is 0.472 and it is almost the same as those of my past experiments.[8] The muzzle velocity must be known before the calculation: it may be a handicap of this method, however, it is sometimes useful when we hope to obtain simply the coefficient for various shapes of shells. When we measure the muzzle velocity of a shell, the instruments must be carefully installed not being disturbed by the gas from the muzzle, because the gas with smoke flows out faster than the shell.

The reason why only Black Powder is used for lifting firework shells is in that it burns very fast even at the atmospheric pressure due to the large value of the vivacity A and raises the pressure in the loading room very rapid, although there is a fairly large clearance between the wall and shell in the barrel. The value of the vivacity of Black Powder is about 200 times as large as that of smokeless powder.

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An Example of Negative Explosives: Magnesium Sulfate/Magnesium Mixture

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ABSTRACT

At the Eleventh International Pyrotechnics Seminar, 1986, in Vail, Colorado, I reported on a study of pyrotechnic mixtures with a theme, "A Concept and the Use of Negative Explosives". A further study has been continued on the same subject as before.

In the former report it was known that magnesium sulfate/magnesium mixture detonates on heating. I studied if it is suitable for the noise mixture of fireworks in place of the ordinary one which contains aluminum and potassium perchlorate and which has long been a cause of serious accidents in the firework industry.

The chemical reaction of the magnesium sulfate/magnesium mixture on detonation is thought to be:

$$MgSO_4 + 4\ Mg \rightarrow MgS + 4\ MgO + 353\ kcal.$$

From several experiments following results were obtained:

(1) The intensity of the explosive noise from the magnesium sulfate/magnesium mixture is almost the same as that from the ordinary aluminum mixture when the weight of the charge of the former is two or two and a half times as large as that of the latter.

(2) The magnesium sulfate/magnesium mixture is far safer on handling than the ordinary aluminum mixture. It was proved by an iron ball dropping test and a fire propagation test.

(3) The tone quality of the noise from the magnesium sulfate/magnesium mixture is mild and superior to that from the ordinary aluminum mixture.

(4) In practical use it is necessary to protect the noise unit which contains the magnesium sulfate/magnesium mixture from moisture.

1. Introduction

The purpose of this study is to discover a safer noise mixture of fireworks than those at present which use aluminum and intensive oxidizers to cause serious accidents in the past.

The important conditions required for a noise mixture are in three points: (1) it must be ignited to detonation without any detonator, (2) it must be safe on handling, (3) the debris must be harmless having no residual fire.

From my former study on a theme "A Concept of Negative Explosives" it is known that the mixture of magnesium sulfate and magnesium detonates by heating in half confined state without detonator, hardly generates sparks by impact and the ash after burnt does not ignite when it is added with water[1]. These characteristics of mixture may well response above requirements. This is the reason why I have selected this type mixture as an example of negative explosives for this study.

2. Fundamental Reactions

The fundamental reactions with mixtures of magnesium sulfate/magnesium may be expressed as follows:

$$(1)\quad MgSO_4 + 4\ Mg \rightarrow 4\ MgO + MgS + 353\ kcal,$$

or

(2) $MgSO_4 \bullet 7\ H_2O + 11\ Mg \rightarrow$
$11\ MgO + MgS + 7\ H_2 + 857$ kcal.

For comparison, with the typical noise mixture, aluminum/potassium perchlorate, the reaction may be:

(3) $3\ KClO_4 + 8\ Al \rightarrow$
$4\ Al_2O_3 + 3\ KCl + 1543$ kcal.

From the theoretical consideration the 1 gram mixture of each type evolves heat of 1.62 kcal with reaction (1), 1.67 kcal with reaction (2) and 2.44 kcal with reaction (3). The values of stoichiometric weight ratio of materials in each reaction are as follows:

(1)	$MgSO_4$/Mg	55.3/44.7
(2)	$MgSO_4 \bullet 7H_2O$/Mg	48.0/52.0
(3)	$KClO_4$/A1	65.8/34.2

3. Materials

Main materials which were used for experiments were as follows:

1) Magnesium sulfate anhydrous, $MgSO_4$: Reagent Class 1, passed 150 mesh, supplied by Kanto Chemicals Co.
2) Magnesium sulfate hydrous (Epsom Salt): Prepared by adding a calculated quantity of water slowly to magnesium sulfate anhydrous. In this occasion a large quantity of heat evolved on mixing. The material thus produced caked to hard grains, which were crushed by an iron muller and passed 80 mesh.
3) Magnesium: Manufactured by Mitsuwa Kinzoku Co., Tokyo, passed 60 mesh.
4) Magnesium: Manufactured by Mitsuwa Kinzoku Co., Tokyo, passed 100 mesh.
5) Aluminum, YP1000: Manufactured by Yamaishi Kinzoku Co., flakes, particle size: 0.05–0.001 mm.
6) Aluminum, P2000: Manufactured by Nakatsuka Kinzoku Co., flakes, particle size: 0.08–0.0005 mm.
7) Sulfur: Manufactured by Hosoi Kagaku Co., passed 100 mesh.
8) Black Powder (small grains): Manufactured by Nippon Kayaku Co., passed 1.2 mm sieve, and remained on 0.4 mm sieve.
9) Black Powder (powdered form): Manufactured by Nippon Kayaku Co., passed 280 mesh.

To compare the effect of the flake aluminum, atomized aluminum was also used:

10) Atomized aluminum, VA1000: Manufactured by Yamaishi Kinzoku Co., particle size: 0.001–0.007 mm.

4. Experimental Determination of the Composition and Form of Mixture

4.1. Preparations

A mixture of magnesium sulfate/magnesium and, for comparison, mixtures of magnesium sulfate/magnalium or aluminum were prepared in powdered and grain form. The weight ratios of component materials were determined by stoichiometric calculations. Materials were weighed out and mixed with each other by hand through a 40 mesh sieve. A part of each mixture was added with a quantity of 10% nitrocellulose solution in amyl acetate and granulated by passing through a punch plate (1.8 mm diameter holes) sieve. Fifteen grams of each mixture were loaded in a round paper capsule and the outside of it was pasted with long pieces of 0.1 mm thick Kraft in eight layers. A piece of boron match (a mixture of 25% boron and 75% potassium nitrate with gum Arabic binder pasted on cotton strands) was inserted into the mixture in the capsule through a small hole of about 3 mm in diameter (Figure 1).

To obtain a standard noise intensity level, two mixtures of another type, which contain aluminum and potassium perchlorate, were prepared:

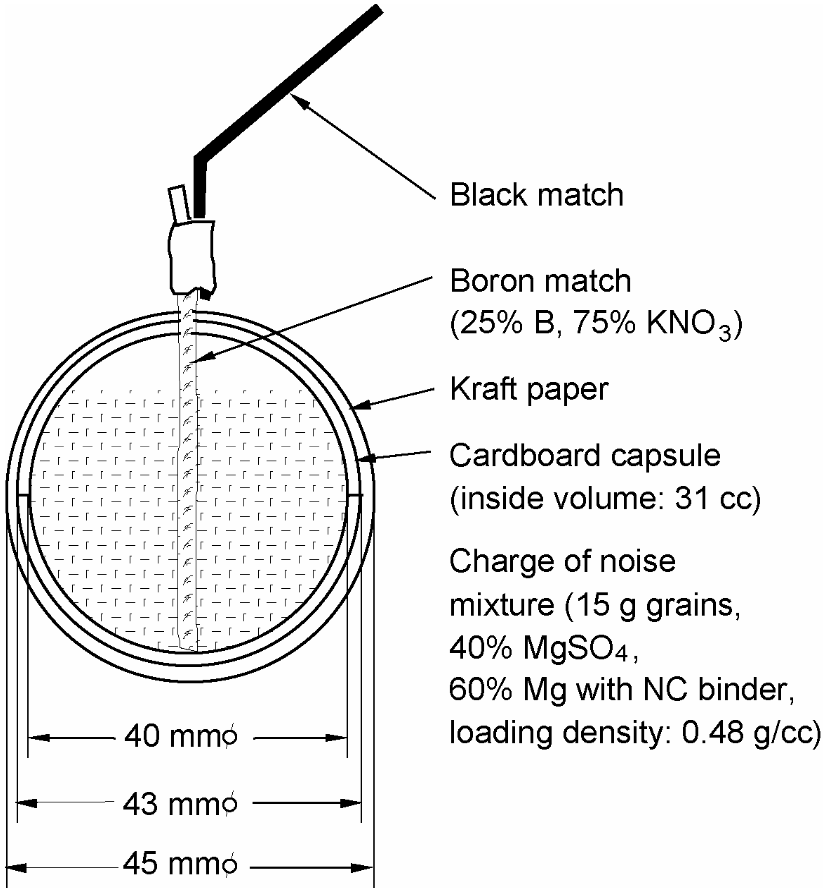


Figure 1. A test sample of capsule type.

S1:	Aluminum, YP 1000	23%
	Potassium perchlorate, passed 150 mesh	64%
	Sulfur	13%
S2:	Aluminum, P 2000	28%
	Potassium perchlorate, passed 150 mesh	72%

S1 and S2 seem to produce almost the same noise effect. S1 or S2 was occasionally used in practice. The apparent specific gravity of S1 was 0.72 g/cc and S2, 0.61 g/cc. The samples of these mixtures were charged in a capsule as before.

4.2. Noise Test with Several Type Mixtures

Each sample was hung with a piece of thin iron wire from a support of a stand 1.3 meters high above ground. A tape recorder, Sony, TC-05M, was placed at a distance of 26 meters from the sample. The sample was ignited and the noise produced was recorded by using a microphone, Sony ECM-909 (condenser type, 100–15,000 Hz). The response of the microphone very much varied depending on the weather conditions, i.e., when cloudy, it was high, but when fair, it was too low. Therefore, the recording level of the recorder was changed according to the weather to obtain adequate results. (Hereafter the data are comparable within one table or figure, but incomparable with those of other table or figure because the dates of recording were different from each other.) It took about two hours to complete a group of tests.

The results are shown in Table 1. The readings of the VU meter of the recorder expressed well our feelings of noise intensity by ears. The standard mixture S1 (No. 0–1, 0–2, 0–3) produced the loudest noise of all. The intensity of the noise from the $MgSO_4$/Mg mixture in grain form (2–1, 2–2, 2–3) is about four decibels lower than that of S1. The tone quality of the

Table 1. The Result of Experiment with Several Type Mixtures.

No.	Composition	Form of mixture	Effect	Response in decibel (VU meter reading)
0-1	23% Al(YP1000), 64% $KClO_4$, 13% S	powder	detonated	0.5
0-2			detonated	1.0
0-3			detonated	1.0
1-1	55% $MgSO_4$, 45% Mg (60 mesh)	Powder	bursted	–3.5
1-2			bursted	–3.0
1-3			not ignited	—
2-1	55% $MgSO_4$, 45% Mg (60 mesh)	Grain	detonated	–3.5
2-2			detonated	–3.0
2-3			detonated	–3.0
3-1	59% $MgSO_4$, 41% Mg/Al (100 mesh)	Powder	not ignited	—
3-2			not ignited	—
3-3			not ignited	—
4-1	59% $MgSO_4$, 41% Mg/Al (100 mesh)	Grain	detonated, but delayed	–3.0
4-2				–3.1
4-3			"	–3.1
5-1	63% $MgSO_4$, 37% Al (atomized, VA1000)	Powder	bursted	—
5-2			detonated	–5.0
5-3			bursted	—
6-1	63% $MgSO_4$, 37% Al (atomized, VA1000)	Grain	not ignited	—
6-2			detonated	–4.5
6-3			not ignited	—
7-1	63% $MgSO_4$, 37% Al (flake, YP1000)	Powder	not ignited	—
7-2			not ignited	—
7-3			not ignited	—
8-1	63% $MgSO_4$, 37% Al (flake, YP1000)	Grain	detonated	–4.0
8-2			not ignited	—
8-3			detonated	–3.0

Note: weight of charge: 15 g.

noise from S1 was sharp and unpleasant, but that from the $MgSO_4$/Mg mixture was mild and musical when we heard them at a distance. Other mixtures had defects in the ignition or detonation, and they were not suitable for the noise mixture.

4.3. Determination of the Weight Ratio of Magnesium Sulfate to Magnesium as a Noise Mixture for Practical Use

Noise intensities from mixtures of several component ratios in grain form were examined with the same sample construction as in Figure 1. The results are plotted in Figure 2.

As Figure 2 shows, the noise intensities are the maximum in the range between 30/70 and 50/50 of magnesium sulfate/magnesium weight ratio. These ratios are lower than the stoichiometric value 55.3/44.7 (see 2). The value of the maximum noise intensity is about 4.5 decibel lower than that of the standard mixture S1.

From the result a magnesium sulfate/magnesium weight ratio of 40/60 was selected for practical use. It could be used not only for noise producing, but also for producing an intensive flash. It has 28 weight percent magnesium in excess which may instantaneously produce a bright flame with help of oxygen in air without

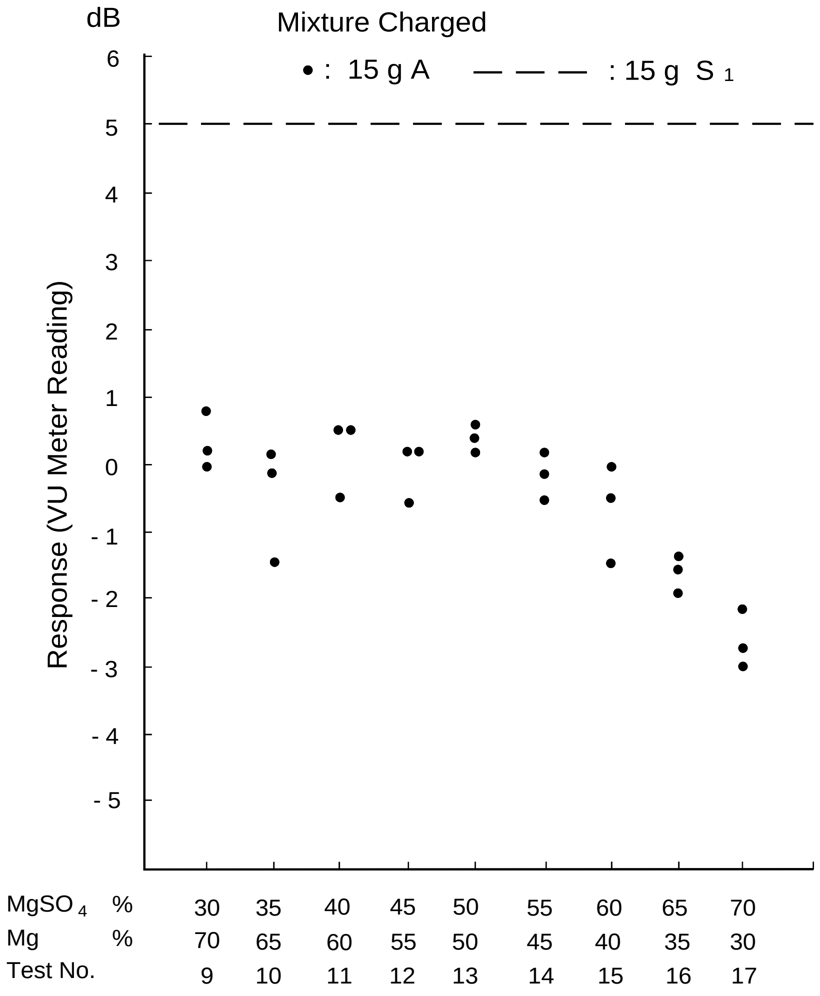


Figure 2. The noise intensities by the response of recorder relative to the weight ratio $MgSO_4/Mg$.

notable decreasing the noise intensity from the maximum.

4.4. Experimental Manufacturing of Magnesium Sulfate/Magnesium Noise Mixture

Composition:

Magnesium sulfate, $MgSO_4$	400 g
Magnesium, Mg	600 g

The mixture was granulated adding 230 grams of 10% nitrocellulose solution in amyl acetate. There were two types in the mesh size of magnesium. With the magnesium passing 60 mesh denoted by symbol A and with that passing 100 mesh, by symbol B. The former tests concerned only with A.

Grains A: Apparent specific gravity: 0.57 g/cc. Grain size distribution by sieving:	weight percent
smaller than 0.175 mm	32
0.355–0.175 mm	56
0.425–0.355 mm	2
0.500–0.425 mm	1.5
0.710–0.500 mm	3
0.850–0.710 mm	1.5
1.000–0.850 mm	2
1.108–1.000 mm	1
larger than 1.108 mm	1

Grains B: Apparent specific gravity: 0.51 g/cc. Grain size distribution by sieving:	weight percent
smaller than 0.175 mm	44
0.425–0.175 mm	42
0.500–0.425 mm	2
0.710–0.500 mm	3.5
0.850–0.710 mm	2.5
1.000–0.850 mm	2.5
1.180–1.000 mm	2.5
larger than1.180 mm	1

The grains of both type converged in size below 0.425 mm, i.e., 85% or more. The microscopic view of these small grains was sketched as it is in Figure 3. Small crystals of magnesium sulfate were firmly fixed on each grain of magnesium. It may be an important condition to obtain a loud noise.

It was found the magnesium sulfate/magnesium mixture makes not so much dust on manufacturing or handling as that from aluminum/perchlorate mixtures.

5. Studies on Practical Use of Mixtures

5.1. The Noise Intensity Relative to the Manufacturing Conditions

The intensities of noise with the strength of capsule, quantity of charge and type of mixtures were examined in comparison with that from the standard mixture S2. The results are plotted in Figure 4.

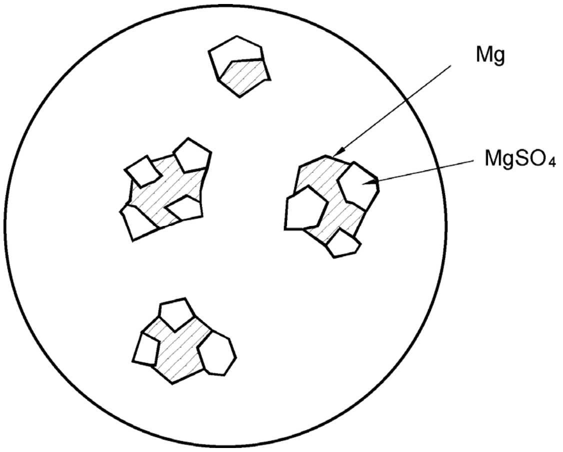


Figure 3. A sketch of small grains of mixture A or B through microscope.

The noise intensity increased with the increase of the strength of capsule. At least six layers of brown Kraft having a thickness of 0.1 mm should be pasted to obtain good effect. The noise effect from the mixture A was the same as that from B.

When the quantity of the charge increased twice as large as that of the original, the noise intensity increased about two decibels. A charge of 30 grams of B type mixture could barely correspond with that of 15 grams of standard S2 in noise effect.

5.2. Practical Noise Units—an Italian Shell Type

On trial Italian shell type units which had a construction shown in Figure 5 were prepared with several weights of charge.

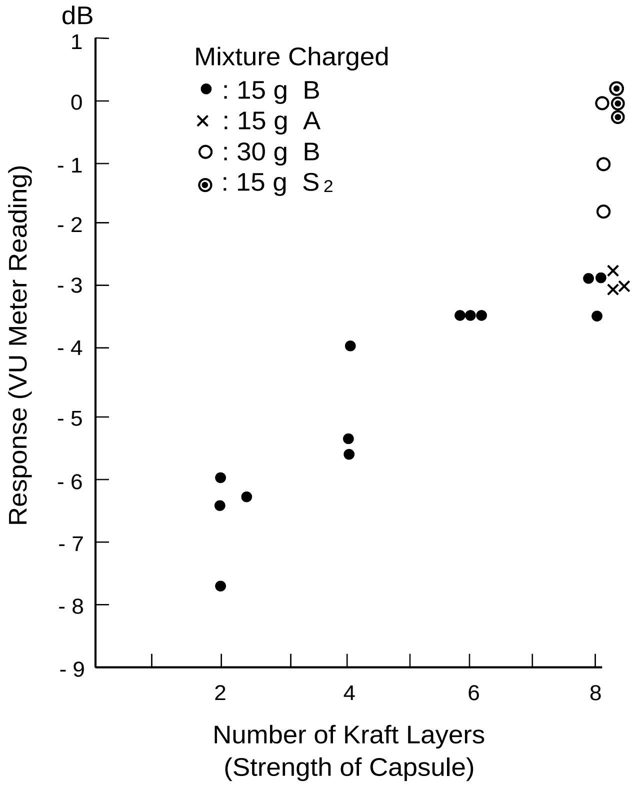
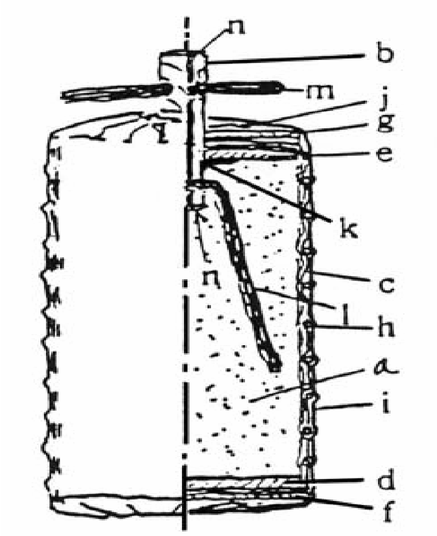


Figure 4. Noise intensities relative to the strength of capsule, quantity of charge and types of mixture A, B and S2.

Here a new type mixture C (40% $MgSO_4 \cdot 7H_2O$/60% Mg) was also used, but it was not effective; it only bursted without detonation.



a: charge of a noise mixture,
b: Bickford fuse,
c: Kraft paper, 0.2 mm thick,
d,e: cardboard disk, 2 mm thick,
f,g: cardboard disk, 1 mm thick,
h: hemp string,
i: Kraft paper, 0.1 mm thick,
j: wheat paste,
k: epoxy resin,
l,m : boron match,
n: pasted with a small quantity of 10% nitrocellulose solution in acetone.

Figure 5. Italian shell type noise unit.

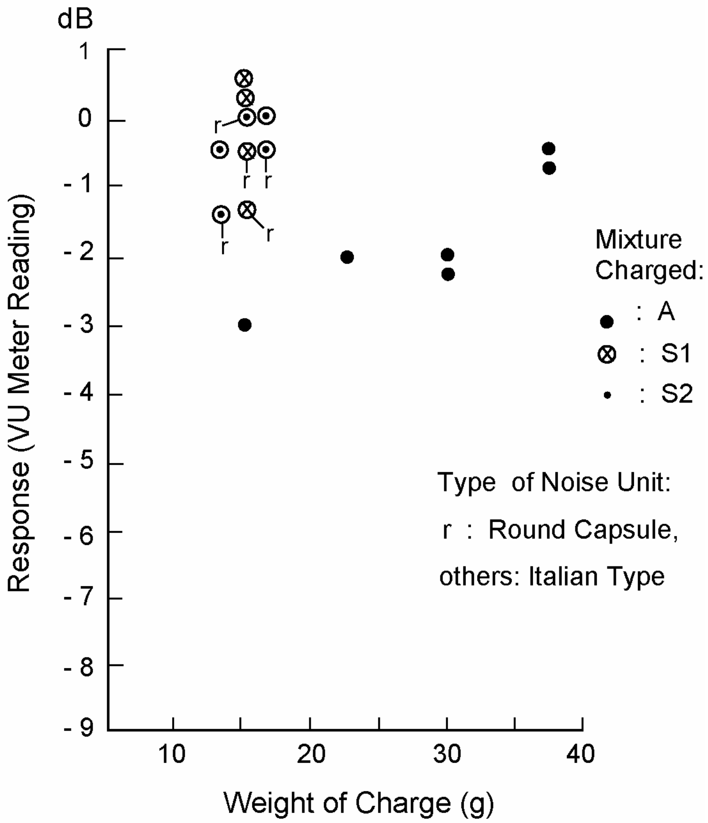


Figure 6. Noise intensities relative to the quantity of charge with Italian shell type noise unit.

The results of experiment are shown in Figure 6.

The noise intensities from standard noise mixtures S1 and S2 were not different from each other regardless of the shapes of capsule, round or Italian type. The noise intensity of 15 grams charge of A was 2.5 decibels lower than that of the standard S1 or S2. To obtain the same noise intensity with mixture A and standard mixture S1 or S2, the charge of A must be increased two or two and a half times as large as that of S1 or S2.

The dimensions which are important for manufacturing noise units are tabulated in Table 2.

Table 2. Dimensions of the Noise Units Relative to Figure 6.

No.	Charge	Composition	Form of Mixture	Type of Unit	Diameter	Length
27	15 g	A ($MgSO_4$/Mg)	grain	Italian	30 mm	52 mm
28	22.5 g	A ($MgSO_4$/Mg)	grain	Italian	35 mm	53 mm
29	30 g	A ($MgSO_4$/Mg)	grain	Italian	37 mm	64 mm
30	32.5 g	A ($MgSO_4$/Mg)	grain	Italian	39 mm	67 mm
31	15 g	C ($MgSO_4 \bullet 7H_2O$/Mg)	grain	Italian	30 mm	57 mm
35	15 g	S1 (standard)	powdered	round	dia. :46 mm	
36	15 g	S2 (standard)	powdered	round	dia. :46 mm	
37	15 g	S1 (standard)	powdered	Italian	32 mm	45 mm
38	15 g	S2 (standard)	powdered	Italian	31 mm	50 mm

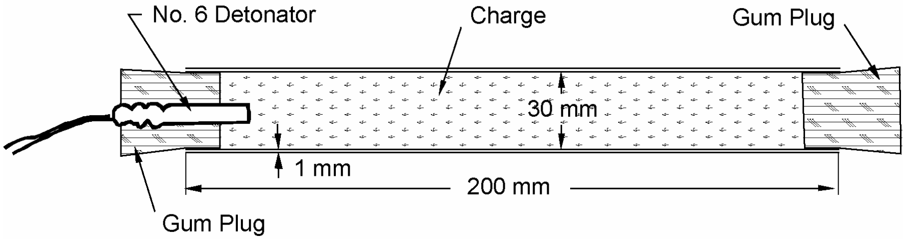


Figure 7. Sample for iron tube test.

With the Italian shell type units it was recommended to use Kraft paper of more than 0.2 mm in thickness to make no residual fire in debris.

6. Safety Test

6.1. Iron Tube Test

Each mixture was loaded in a seamless iron tube of 30 mm outside diameter, 200 mm long and a wall thickness of 1 mm and the one end was initiated with a No. 6 detonator (Figure 7) on the ground. The results are shown in Table 3 and Figure 8.

6.2. Fire Propagation Test

On manufacturing noise units the most dangerous operation may be the handling of an unconfined noise mixture. Generally it is thought that an accident occurs when a small fire is produced at the smallest part of the mixture by a shock, friction or by other heat sources and then the fire quickly propagates to all parts of the mixture. Therefore, the propagation from the original small fire must be well studied. When no propagation occurs, the accident never occurs even if the small fire is produced.

Table 3. The Result of Iron Tube Test.

No.	Composition	Charge	Result
39	S2 (28% Al/72% $KClO_4$)	69 g	Terribly detonated forming a crater, 150 mm wide, 280 mm long and 70 mm deep on the ground. The tube was broken into small splinters.
40-1	A (40% $MgSO_4$/60% Mg)	64 g	Mildly detonated without forming any crater, no splinter. The tube was torn along the all length.
40-2	A (40% $MgSO_4$/60% Mg)	64 g	Mildly detonated without forming any crater, no splinter. The tube was torn 160 mm along the length.
41	C (40% $MgSO_4$•$7H_2O$/40 % Mg)	60 g	Seams half detonated, no crater or splinter. The tube was torn 115 mm along the length.
42	Blank (100% Mg)	76 g	Not detonated, the tube was torn 60 mm long along the length by the action of No. 6 detonator.

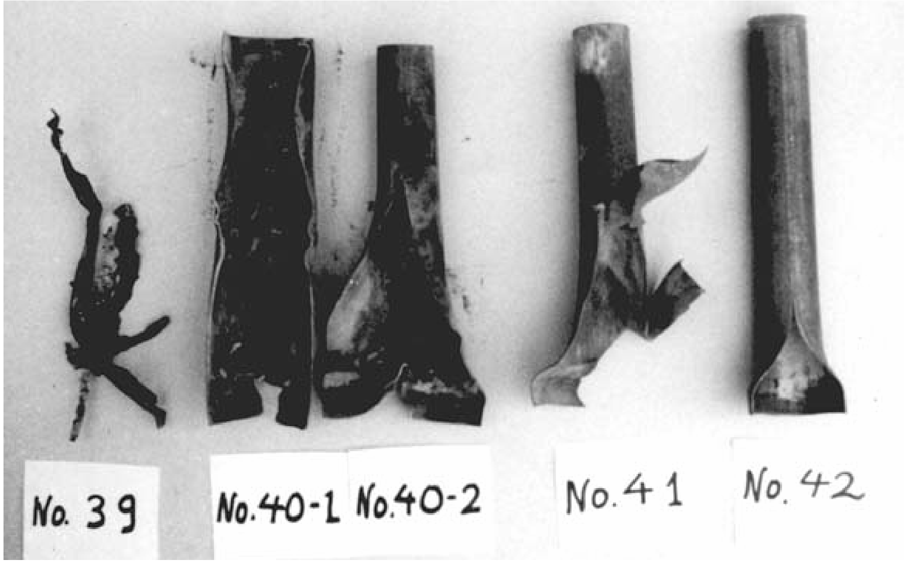


Figure 8. The debris obtained after the iron tube test.

To test the fire propagation the following simple method was used (Figure 9). A quantity of a sample mixture (about 2 grams) was spread in a shape of a thin disk, 8 cm in diameter and having a possibly uniform thickness of 1 mm, on a steel plate of 6 mm thick which was set on a concrete base. An iron ball, 48.6 mm in diameter and weighed 440 g, was dropped onto the sample disk from a height of 2 meters and the effect was observed.

Then the sample disk was prepared again and an end of a piece of black match was placed on the disk so that a length of about 20 mm of the match was contacted with the mixture. The black match was ignited and the fire propagation was observed.

The results are shown in Table 4.

Table 4. The Result of Fire Propagation Test.

By dropping an iron ball					By a fire from black match					
No.	S1	S2	A	C	No.	S1	S2	A	C	Symbols:
1	●	×	×	×	11	∇	∇	×	×	× : no ignition
2	×	×	×	×	12	∇	∇	×	∇	
3	●	⊗	×	×	13	∇	∇	◎	×	∇ : smoothly propagated
4	●	×	×	×	14	∇	∇	◎	∇	
5	●	×	×	×	15	∇	∇	◎	×	◎ : actively propagated
6	●	●	×	×	16	∇	∇	◎	×	
7	●	×	×	×	17	∇	∇	×	×	⊗ : a small fire appeared, but not propagated
8	●	×	×	×	18	∇	∇	◎	×	
9	●	●	×	×	19	∇	∇	◎	×	● : detonated
10	●	●	×	×	20	∇	∇	◎	×	

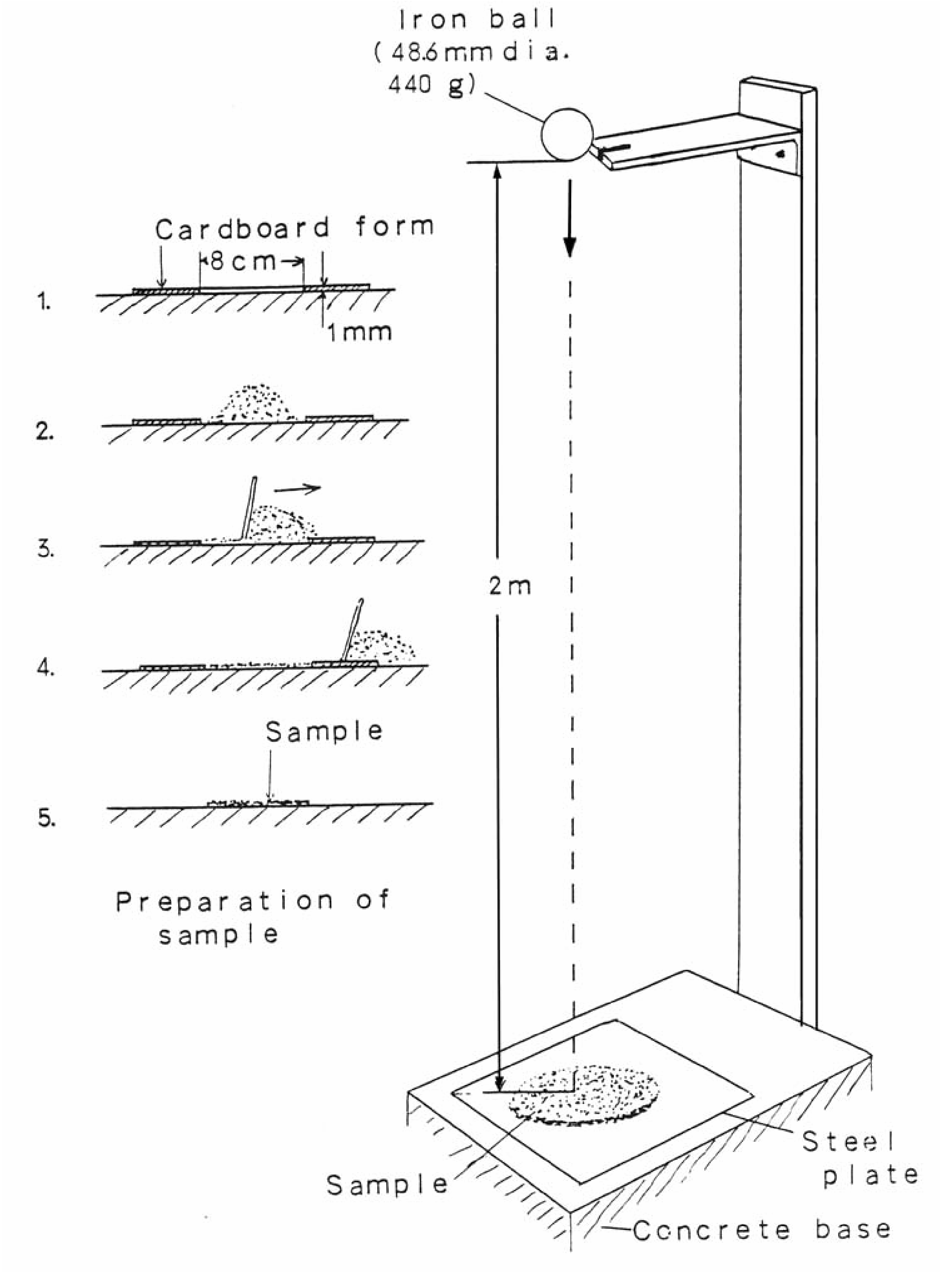


Figure 9. Fire propagation test apparatus.

The standard mixture S1 and S2 which contain aluminum mostly detonated with a loud noise and without remainder when the ball was dropped onto the disk. However, when the disk was ignited by black match, they only smoothly burned. On the contrary, the mixture A and C which contained magnesium sulfate and magnesium neither detonated nor burned when they were struck by the iron ball. However, they were ignited by the flame of black match. A actively burned and C smoothly burned.

7. Preservation Test

About 5 grams of mixture A which contained magnesium sulfate anhydrous and that of mixture C which contained magnesium sulfate hydrous both in grain form were weighed out. They were placed in a room in unconfined state. Each weight was measured at intervals of several days. In appearance the mixtures did not look wet, but dry even though they slowly absorbed moisture in the air. The weather during the test was not good, rainy days continued and the room temperatures were between 5 and 10 °C. The results are shown in Figure 10.

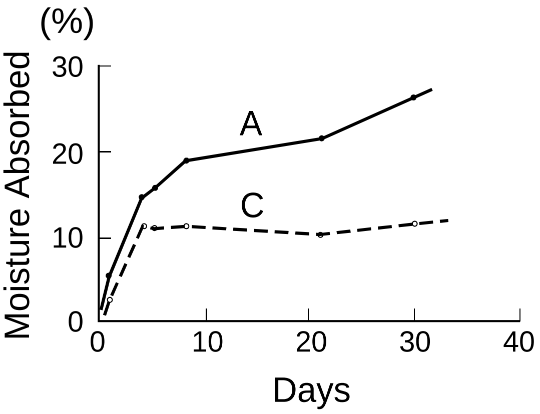


Figure 10. The result of moisture absorption test.

The value of noise absorption increased with time, especially with mixture A. In the literature cited below[2] it said that $MgSO_4•7H_2O$ is stable between temperatures of 1.8 to 48.3 °C and to obtain $MgSO_4$ it is necessary to raise the temperature to more than 200 °C. Of course the large increasing of absorption of moisture with the mixture A was due to $MgSO_4$ contained. It must be avoided by some adequate method, e.g., by packing the noise unit with aluminum or tin foil, because the water absorbed into the mixture would disturb the noise producing. Mixture C could not be used as a noise composition, although it might produce reaction heat far more than A (see 2 and 5.2).

8. Miscellaneous Experiments

8.1. Magnesium Sulfate/Magnalium Mixtures

The mixtures of this type were examined with compositions from the ratio ($MgSO_4$/ Mg/Al) 30/70 to 70/30 by the same method as in Section 5.2. The maximum intensities laid between the ratios 40/60 to 60/40. The noise intensity seemed to be considerably lower than that from the magnesium sulfate/magnesium mixtures. The ignition delayed especially in the range of composition between the values 55/45 and 70/30.

8.2. Magnesium Sulfate Hydrous/Magnesium Mixture ($MgSO_4$ •$7H_2O$/Mg) as a Propellant

This experiment was out of the purpose, but it was carried out for reference, because the mixture of this type theoretically evolves a large amount of reaction heat and H_2 gas which may be effective as a propellant.

A firing test was carried out by using the same mortar as used before[1]. The projectile was made of bronze and weighed 400 grams. As the propellant the mixture C (40% $MgSO_4•7H_2O$/60% Mg) was used. The propellant charge for one firing was 5 grams. The flight distance of the projectile with an angle of elevation of 45° was 43.6 meters in average of 10 tests. For comparison, the projectile fired with 1 gram charge of a Black Powder on sale (small grains, 0.4–1.2 mm). The flight distance was 73.4 meters in average of 2 tests. The values of force of propellant are roughly compared with each other by the following calculation:

$$\frac{\text{Force of mixture C}}{\text{Force of B. P.}} = \frac{\text{Flight distance by mixture C}}{\text{Flight distance by B. P.}} \times \frac{\text{Charged weight of B. P}}{\text{Charged weight of mixture C}} =$$

$$: \frac{43.6}{73.4} \times \frac{1}{5} = \frac{1}{8} (\text{B. P.: black powder})$$

9. Discussion and Conclusions

1) To obtain the same noise effect as that of ordinary aluminum/perchlorate mixtures by using the magnesium sulfate/magnesium mixture, it is necessary to use two or two and a half times as large as the quantity of the unit charge of the former. In this case the volume of the latter noise unit becomes 2.0 or 2.4 times as large as that of the former from the data in Table 2.

   The magnesium sulfate/magnesium mixture gradually absorbs moisture in the air when it is stored. This may disturb the producing of noise. The noise unit should be covered with a tin or aluminum foil, or the mixture should be loaded in a plastic capsule, which produces no dangerous debris or splinters, to prevent the unit from absorbing moisture.

   These are the main defects of the mixture of this type.

2) A large merit of the magnesium sulfate/magnesium mixture is that it is far safer than the ordinary aluminum/potassium perchlorate mixture in handling in an unconfined state.

3) Even when a relatively light shock is given to the aluminum/perchlorate mixture which has been spilt on the floor, a small fire may occur at the shocked point and the fire propagates instantaneously to the all part with a terrible detonation. On the contrary, such a reaction does not occur by the action of the flame. Generally, the serious accidents with the ordinary noise mixture may come from such rather curious characteristics of them.

   On the contrary, magnesium sulfate/magnesium mixture is very difficult being detonated by shock in such an unconfined state. In confined state the magnesium sulfate/magnesium mixture can detonate, but it does not produce terribly dangerous small splinters of its container.

4) Another merit of the magnesium sulfate/magnesium mixture is that it produces little dust on handling. The ordinary aluminum/perchlorate mixture always makes dust unavoidably, which soils workers and the room and which have a risk of a dust explosion.

5) The tone quality of the noise from magnesium sulfate/magnesium mixture is mild. It may be a merit of the mixture of this type for practical use. On the contrary, the noise from the ordinary aluminum/potassium perchlorate mixture gives us a very sharp and fierce feeling.

6) Although mixtures of magnesium sulfate with metals, aluminum in flake or atomized type and magnalium, other than magnesium were examined, their noise was too low to use practically or they were not easily ignited.

7) The mesh size of magnesium had no influence on the noise intensity when the magnesium was sieved by 60 or 100 mesh.

8) The maximum intensity of noise was obtained from the weight ratio of magnesium sulfate/magnesium between the ranges of 30/70 to 50/50 irrespective of the stoichiometrical value 55/45.

9) The mixture of magnesium sulfate/magnesium does not produce a good noise when it is not granulated.

10) To obtain a good noise effect with the magnesium sulfate/magnesium mixture, the capsule strength must be practically large.

11) An Italian shell type capsule should be constructed by rather thick Kraft paper, e.g., 0.2 mm in thickness, to avoid residual

fire in the debris when the magnesium sulfate/magnesium mixture is used.

12) The mixture which consists of magnesium sulfate hydrous, $MgSO_4 \bullet 7H_2O$, and magnesium is not useful for noise mixture because the noise intensity from this mixture is too low. It could be used for other purposes.

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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

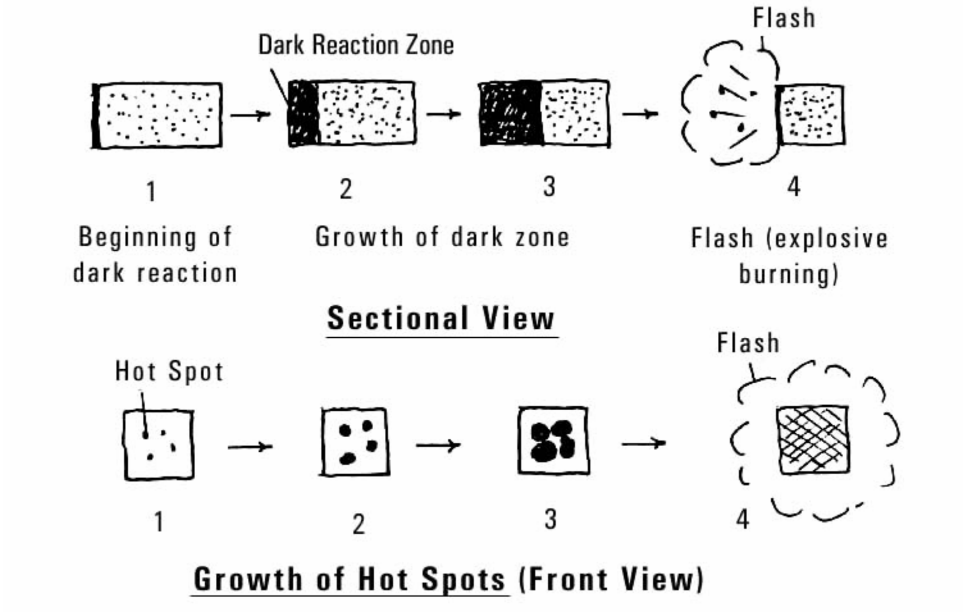

Figure 1. The principle of one cycle of strobe reaction.

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.

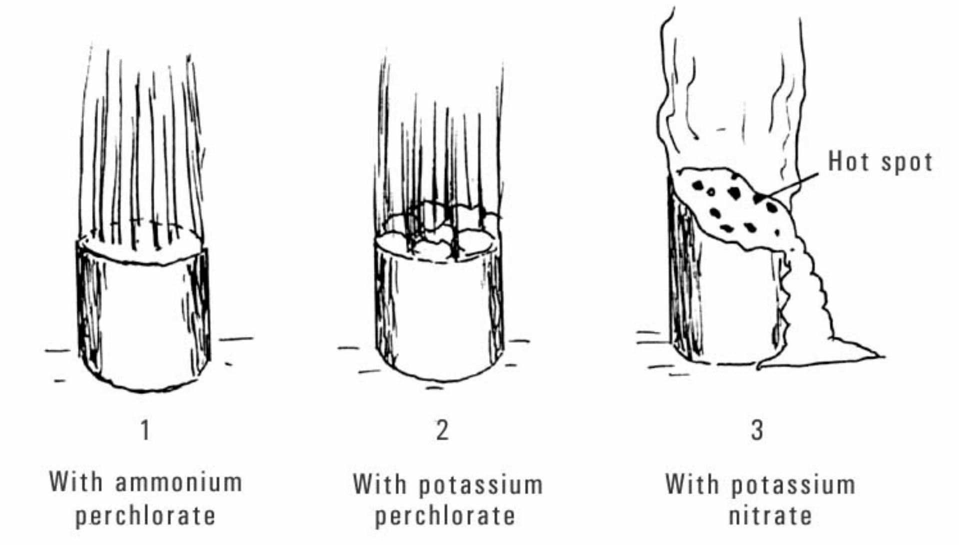

Figure 2. Burning looks of three type sample specimens.

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'.

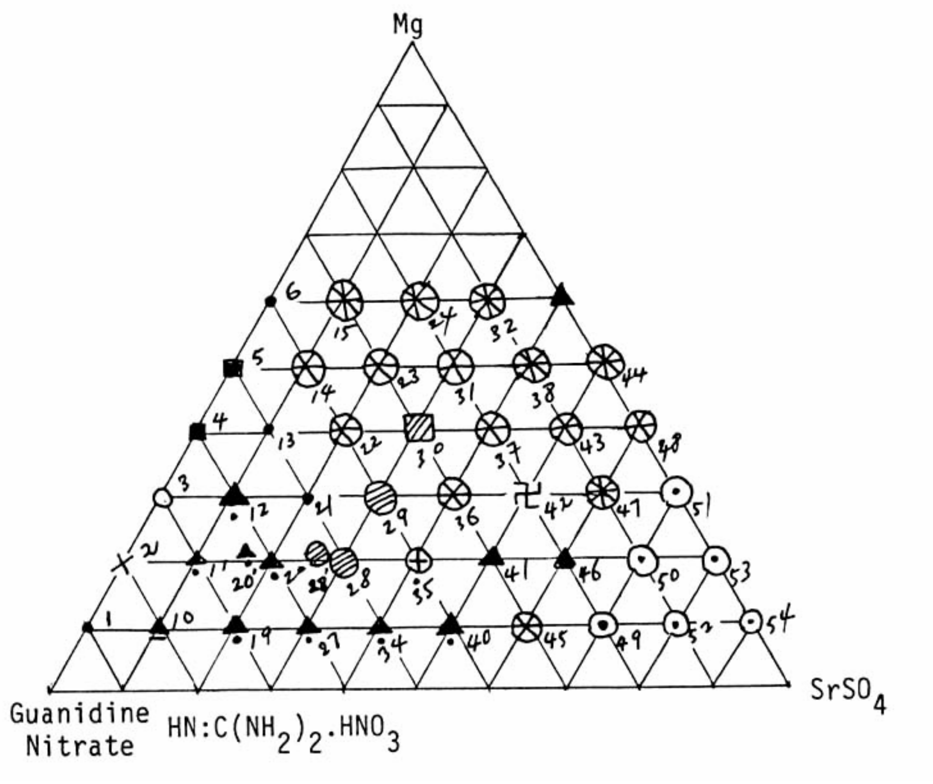

Figure 3. Burning characteristics of base compositions of strobe light.

Symbols:	●:	Only smolders.	⊗:	Continuous burning.
	○:	Only burns.	⊛:	Continuous and intensive burning.
	■:	Very slowly blinks.	◍:	Blinks with a large flame.
	♦:	Blinks not sharply.	▨:	Blinks without sharp cut.
	⏏:	Irregularly blinks.	⊕:	Burns, then smolders.
	▲:	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, $HN:C(NH_2)_2 \cdot H_2O$	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, $CaSO_4 \cdot 1/2H_2O$	—	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.

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The Surface Explosion of Pyrotechnic Mixtures

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ABSTRACT

In the past we sometimes observed a fairly large burning star caused an explosion with a loud noise at the very moment when it fell onto the ground. The star did not explode totally, but only with the thin surface layer. The burning surface layer of the star may be very sensitive to shock because of the high temperature. This phenomenon is here called the "surface explosion."

The objective of this paper is to investigate the surface explosion by experiments. It may be very important to make clear the mechanism of the transition from burning to explosion or detonation not only with pyrotechnic mixtures, but also with general explosives, especially to avoid accidents.

The mechanical sensitivity of the burning surface layer was examined by dropping an iron ball onto it with consolidated mixtures of ordinary stars and illuminants, etc. Most of them showed a higher sensitivity than that of a standard mixture called red explosive at ordinary temperatures.

Using small rocket engines, propellant of potassium chlorate and potassium perchlorate comparing with that of ammonium perchlorate were examined. The former two caused the surface explosion or a perfect detonation when ignited and the rocket engines were broken, and only the propellant of ammonium perchlorate worked well.

The phenomenon of the surface explosion was discussed in combination with a past accident.

Introduction

The objective of this paper is to investigate the surface explosion which sometimes occurs at the burning surface layer of a pyrotechnic mixture. We see a brightly burning star explodes with a loud noise when it falls onto the ground. The star explodes not entirely, but only at the burning surface layer and the fire goes out with the explosion leaving an unburnt part. In this case it is clear that the surface explosion occurs by a mechanical shock. Namely, the burning surface layer should be very sensitive due to a high temperature. Here, I intend to make clear the shock sensitivity of the burning layer of several ordinary pyrotechnic mixtures comparing with that of red explosive: 63% potassium chlorate + 27% realgar as a standard[1]. The red explosive is one of the most sensitive mixtures of fireworks. Experiment 1 concerns this problem.

Further, a question may arise, how largely the surface explosion is influenced by pressure when it is in a confined state. To answer this question, several fundamental compositions were tested by small rockets. Experiment 2 concerns this problem.

Experiment 1. Shock Sensitivity

The shock sensitivity of the burning layer of various consolidated mixtures was examined by dropping an iron ball from a height of one meter (except few mixtures) onto the burning surface of a sample star.

The sample compositions of the mixtures are tabulated in Table 1. Each mixture of about 60 grams was pressed into a Kraft tube of 34 mm in diameter and a thickness of 0.6 mm using a press and formed with a pressure of 960 kg/cm^2. Before the pressing, the mixtures of Group 1 and 2 in Table 1 were added with a small amount of water until they become slightly wet to help the consolidation. These stars were dried for 20 days at room temperatures after the pressing.

The red explosive was prepared as a standard mixture. 31.5 grams of potassium chlorate and 18.5 grams realgar powder were separately sieved passing a 100 mesh sieve and then they are mixed gently by hand. Then, the mixture was sieved passing a 60 mesh sieve three times. This red explosive was used for the experiment in powdered state.

Table 1. Sample Compositions for Experiment 1.[2]

Group 1	No. 1 Red star	No. 2 Yellow star	No. 3 Green star	No. 4 Blue star
Potassium perchlorate (250 mesh)	66%	68%	47.2%	60.8%
Barium nitrate (150 mesh)	—	—	28.3	—
Accroides resin (100 mesh)	13	18	14.2	9.0
Strontium carbonate	12	—	—	—
Sodium oxalate	—	7	—	—
Basic copper carbonate	—	—	—	12.3
Chlorinated isoprene rubber	2	—	4.7	13.1
Lamp black	2	2	—	—
Glutinous rice starch	5	5	5.6	4.8

Group 2	No. 5 Red star brilliant	No. 6 Yellow star brilliant	No. 7 Green star brilliant	No. 8 Flare star
Potassium perchlorate (250 mesh)	30%	45%	16%	—%
Strontium nitrate (100 mesh)	20	—	—	—
Sodium nitrate (80 mesh)	—	—	—	50
Barium nitrate (200 mesh)	—	—	42	—
Glass powder	—	13	—	—
Magnesium (80 mesh, coated with 5% $K_2Cr_2O_7$)	30	30	25	50
Chlorinated isoprene rubber	18	10	15	—
Lamp black	2	2	2	—

Group 3	No. 9 Silver wave %	No. 10 Golden wave %	No. 11 Rocket(black powder type) %
Potassium perchlorate (250 mesh)	50	—	—
Potassium nitrate (200 mesh)	—	37	60
Aluminum, flake (80 mesh)	50	47	—
Antimony trisulfide (80 mesh)	—	9	—
Sulfur (100 mesh)	—	—	10
Charcoal (200 mesh)	—	—	30
Boric acid (add. %)	—	1	—
Glutinous rice starch (add. %)	7	6	—

Four sizes of iron ball were prepared to give a shock onto a burning sample star:

	Diameter	Weight
Ball 1	76.2 mm	1.820 kg
Ball 2	63.5	1.045
Ball 3	50.3	0.540
Ball 4	38.2	0.230

The test apparatus was installed outdoors as it is seen in Figure 1.

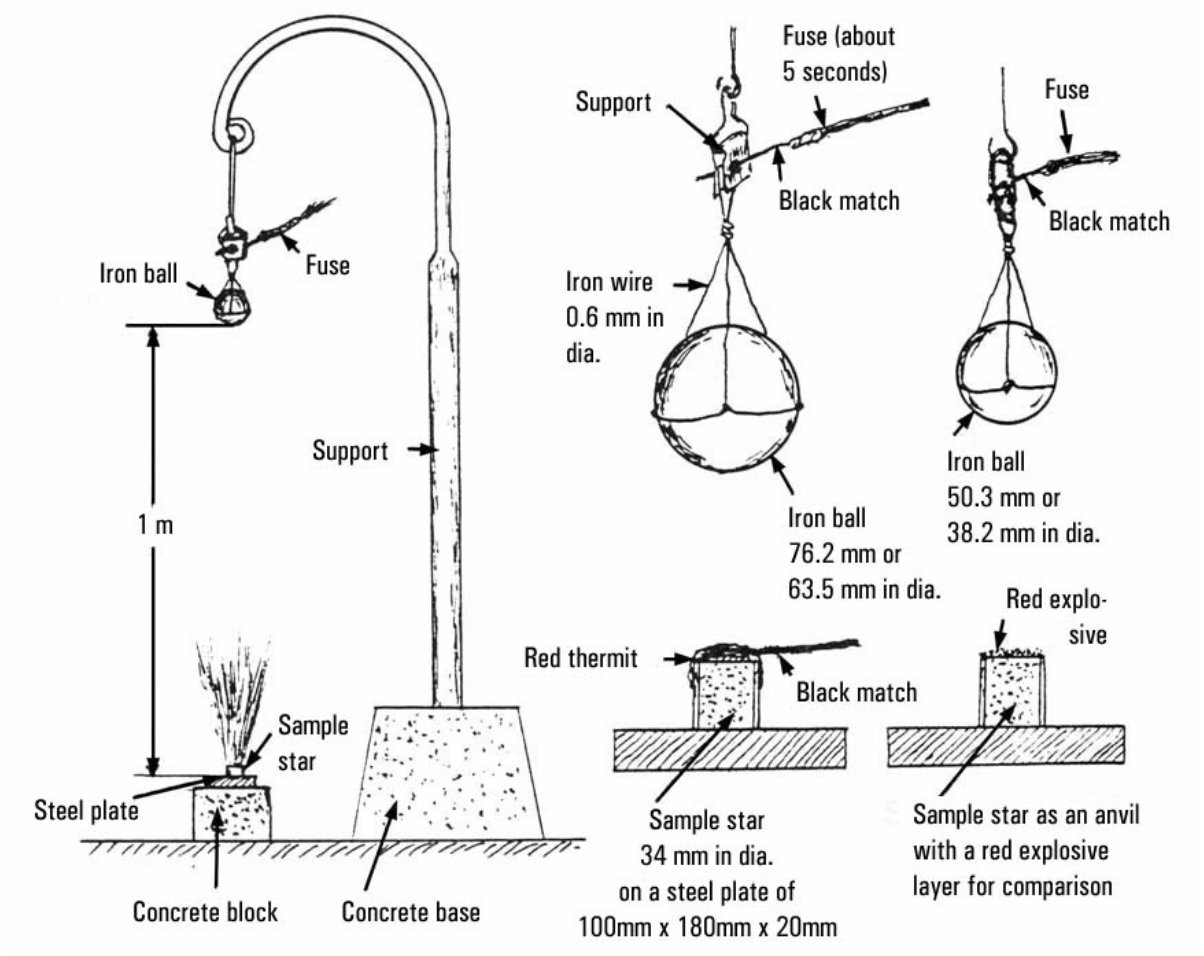


Figure 1. Apparatus for testing sensitivity of burning surface layer by dropping an iron ball onto a burning sample star.

When the end of fuse was ignited, the fire began to proceed towards the support of the ball. At once, the sample star was ignited with black match attached to the star and began to burn. After a proper time delay, which was beforehand adjusted by the length of the fuse, reached the support. The ball was cut off from the support and fell down onto the burning surface of the star to give a shock. The test was repeated four times for each mixture changing the weight of the iron ball for each new sample star on each trial.

Then a new star of the same mixture was placed on the same position as before. About one gram of the red explosive as the standard for comparison was placed on the surface of the star as it is shown in Figure 1. The largest iron ball was released onto the red explosive on the surface of the star by the same method as above. In this case, the condition was the same as if the burning layer was replaced by the layer of the red explosive.

The star remaining at the burning or placed under the layer of the red explosive plays the same role of a buffer against the shock. On the other hand, the shock sensitivity of the red explosive without any buffer action was examined: the largest iron ball was dropped from a height of 18 cm onto an about 1 mm layer of the red explosive placed on a steel plate (100 mm x 180 mm x 20 mm) for seven times.

The results are shown in Table 2.

Table 2. The Results of Shock Sensitivity Test by Dropping an Iron Ball onto the Burning Surface of Stars.

Type of composition	Specific weight (g/cm^3)	Burning time★ (s)	Height of ball (m)	Effect of dropping iron ball					
				onto burning star				onto red explosive with anvil star	
Weight of ball (kg) ➔➔➔				1.820	1.045	0.540	0.230	1.820	1.820
Group 1									
No. 1 Red star	2.03	12.0	1.00	◎	○	○	×	◎	—
No. 2 Yellow star	1.73	8.2	1.00	◎	○	×	×	—	—
No. 3 Green star	2.21	39.8	0.30	○	○	×	×	×	—
No. 4 Blue star	2.09	23.0	0.30	×	×	×	×	×★★	◎★★
Group 2									
No. 5 Red star brilliant	2.02	20.0	1.00	◎	◎	○	○	◎	◎
No. 6 Yellow star brilliant	1.81	12.6	1.00	◎	◎	○	Δ	×	×
No. 7 Green star brilliant	2.08	15.7	1.00	◎	◎	○	Δ	×	×
No. 8 Flare star	1.75	15.8	1.00	◎	◎	◎	○	×	×
Group 3									
No. 9 Silver wave	2.28	3.8	1.00	◎	◎	○	Δ	×	◎
No. 10 Golden wave	2.24	7.3	1.00	◎	◎	○	○	×	×
No. 11 Rocket	1.57	7.0	1.00	×	—	—	—	×	—

Standard red explosive with no anvil star, but on a steel plate with 1.820 kg ball from a height of 0.18 m: ◎◎◎×◎×◎

Symbols:
- ◎: The burning layer exploded with a loud noise and the fire was extinguished,
- ○: exploded with smaller noise than the former and the fire was not extinguished,
- Δ: exploded in small part with small noise and the fire continued without disturbance,
- ×: did not explode,
- —: not tested.
- ★: Burning time when no test,
- ★★: the height of ball was 1 m.

Table 3. Sample Rocket Propellant Compositions for Experiment 2.

	Potassium chlorate (200 mesh) %	Potassium perchlorate (250 mesh) %	Ammonium perchlorate (200 mesh) %	Polyester %	Accroides Resin %	Dextrin (additional) %
A	76	—	—	24	—	—
B	76	—	—	—	24	3
C	—	74	—	26	—	—
D	—	74	—	—	26	3
E	—	—	78	22	—	—
F	—	—	78	—	22	3

Experiment 2 Pressure Sensitivity

It is anticipated that the sensitivity of the burning layer of a consolidated mixture is raised with the burning pressure. The effect was examined with several fundamental compositions using small rocket engines.

The interior pressure P is denoted as:

$$P = A(Ab/At)^B$$

where

Ab is the burning surface area of the propellant,

At the nozzle throat area,

A and B are the constants due to the composition of the propellant.[3]

When the ratio Ab/At is a proper value, the rocket propellant will burn smoothly under the pressure P. However we saw sometimes a

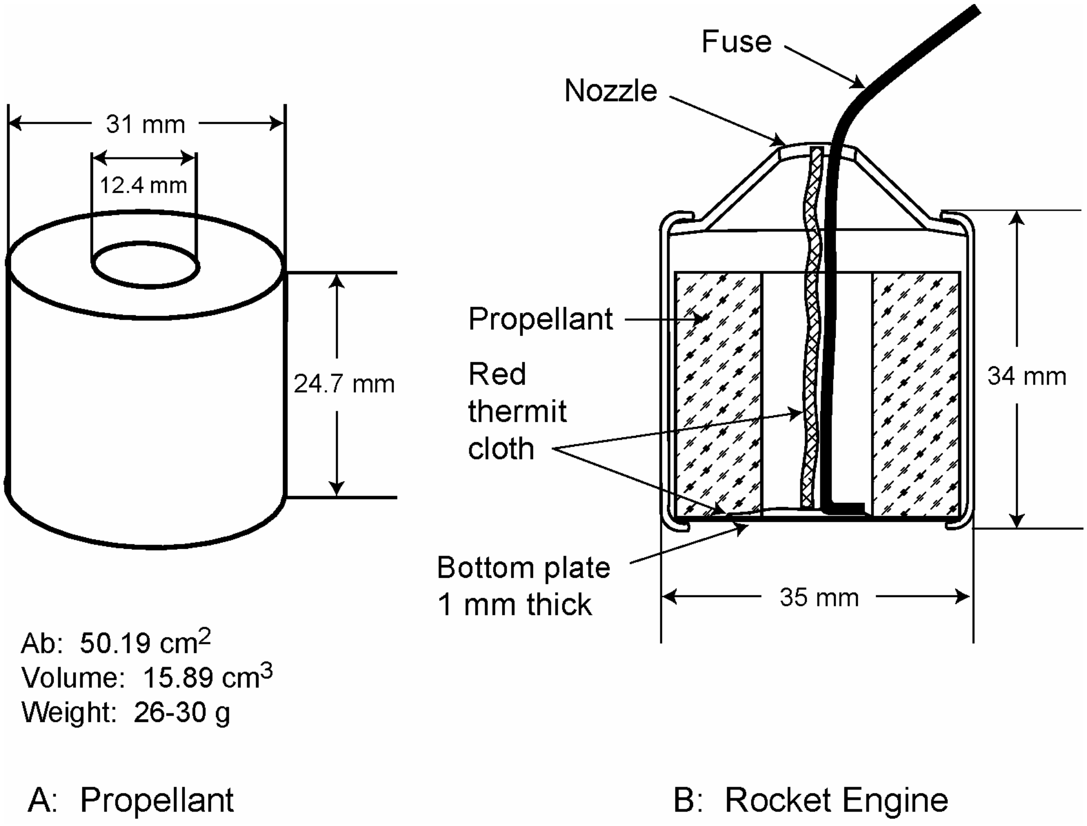


Figure 2. Sample rocket propellant and engine.

rocket engine exploded leaving a remainder of the propellant which was burnt only with the thin surface layer. This may be a phenomenon of the surface explosion.

Six types of propellant composition were selected as the samples as shown in Table 3.

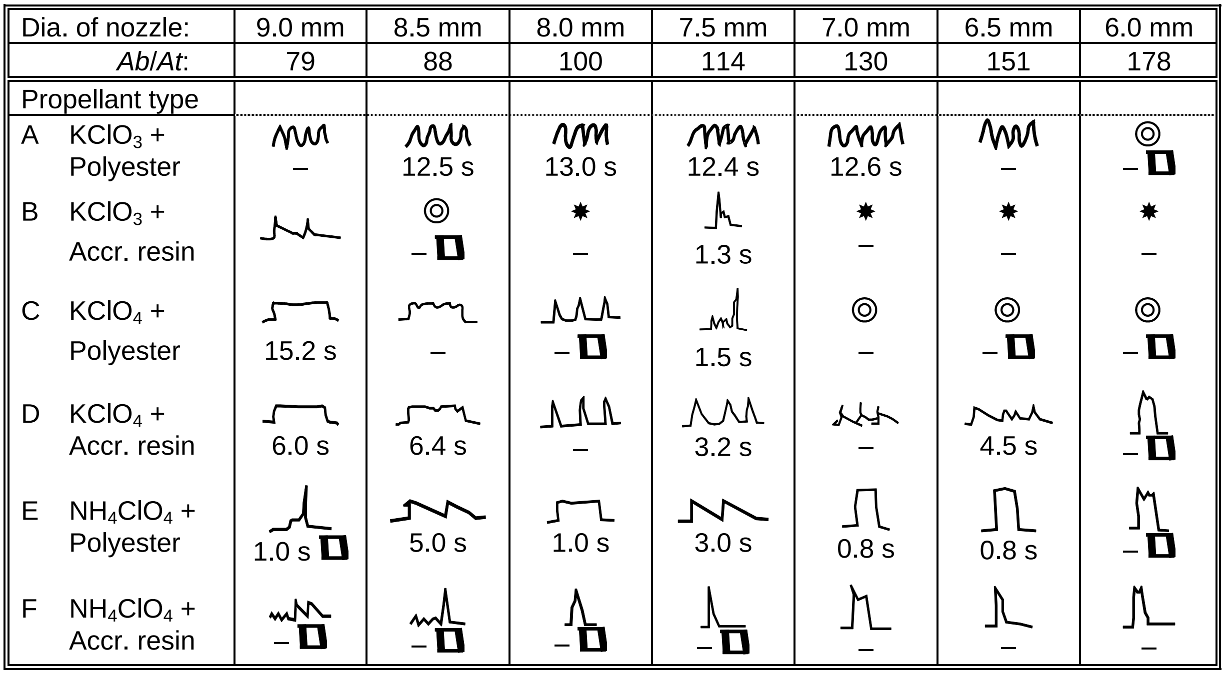
All the compositions were formed into a tubular shape of about 31 mm outside diameter, 12.5 mm inside diameter and about 25 mm long. A, C or E was consolidated with polyester as a binder. B, D or F was added with a small quantity of water until slightly wetted and consolidated by a press under a pressure of 1210 kg/cm^2, and dried at room temperatures for a week. Each propellant was loaded into a small engine as it is seen in Figure 2. All the parts of engine were made of iron except the propellant and ignition materials.

As it is seen in Table 4, in the *Ab*/*At* range from 79 to 178 only five tests showed the surface explosion. They concerned the propellant types A, B and C which contain potassium chlorate or potassium perchlorate. The thickness of the exploded burning surface layer is roughly calculated from the weight difference between the original and the remainder ΔW:

$$\Delta t \;=\; \Delta W / S\delta,$$

where Δt is the thickness of the burnt surface layer, S the surface area of propellant, δ the specific density. The results of calculation are shown in Table 5.

Table 4. The Results of Burning Small Rocket Engines Changing the Values of *Ab*/*At*.



Dia. of nozzle:	9.0 mm	8.5 mm	8.0 mm	7.5 mm	7.0 mm	6.5 mm	6.0 mm
Ab/*At*:	79	88	100	114	130	151	178
Propellant type							
A KClO$_3$ + Polyester	–	12.5 s	13.0 s	12.4 s	12.6 s	–	◎ – ▣
B KClO$_3$ + Accr. resin		◎ – ▣	✸ –	1.3 s	✸ –	✸ –	✸ –
C KClO$_4$ + Polyester	15.2 s	–	– ▣	1.5 s	◎ –	◎ – ▣	◎ – ▣
D KClO$_4$ + Accr. resin	6.0 s	6.4 s	–	3.2 s	–	4.5 s	– ▣
E NH$_4$ClO$_4$ + Polyester	1.0 s ▣	5.0 s	1.0 s	3.0 s	0.8 s	0.8 s	– ▣
F NH$_4$ClO$_4$ + Accr. resin	– ▣	– ▣	– ▣	– ▣	–	–	–

The symbols in Table 4 mean as follows:

◎ surface explosion, ✸ perfect explosion (detonation).

Curves (they are written by imagination from the burning sound from the sample rockets as the pressure curves):

: vibratory burning, the frequency is thought to be 4–6 times per second,
: smooth burning,
: irregular burning.

The numbers under the symbols denote the burning times of propellant. The other symbol ▣ denotes only the thin surface layer of the propellant burnt and the residual part remained.

Table 5. Calculated Values of Thickness of the Burnt Layer at the Surface Explosion.

	Propellant type	Ab/At	ΔW (g)	S (cm^2)	δ (g/cm^3)	Δt (mm)
A	$KClO_3$ + Polyester	178	3.5	50.2	1.75	0.4
B	$KClO_3$ + Accroides resin	88	4.5	50.2	1.75	0.5
C	$KClO_4$ + Polyester	130	4.5	50.2	1.95	0.4
		151	4.0	50.2	1.95	0.4
		178	3.0	50.2	1.95	0.3

The interior pressure of the rocket, when the surface explosion occurred, was roughly calculated from the deformation of the bottom iron plate (1 mm thick and 33.8 mm in diameter) as about 30 kg/cm^2.

The sample propellants in unconfined state burnt smoothly in the air. The burning time of each sample was A: 15 s, B: 4.5 s, C: 19 s, D: 9.2 s, E: 5.0 s, F: 5.5 s.

Discussions

When a shock is given to the burning surface of a consolidated mixture, an explosion occurs (Table 2). In this case, the part which causes the explosion is only a thin burning layer of the surface.

As it is seen in Table 2, when using 1.82 kg iron ball, the fire is entirely extinguished with a loud noise. However, with 0.54 kg ball the fire continues, or even when extinguished, it is soon recovered. Therefore, it is seen that the outbreak and propagation of the surface explosion are strongly influenced by the intensity of shock and width of shocked area.

In Table 2, the mixtures from No. 5 to No. 10 which contain a metal powder, magnesium or aluminum, are the most sensitive and have the highest propagation effect as a surface explosion. No. 1 or No. 2 which contain no metal powder is somewhat less sensitive than the former. Only an exception is No. 11, a rocket propellant of Black Powder type: it does not cause surface explosion even when struck by the 1.82 kg ball. Thus, the shock sensitivity of the burning surface of a consolidated mixture depends largely upon the type of the mixture, and the metal powder accelerates the shock sensitivity. (The effect of No. 3 Green star or No. 4 Blue star cannot be compared with those of others because the dropping height of ball is not 1.00 meter, but 0.3 meters, except marked with ★★.)

In Table 2, the shock sensitivity of mixtures relative to the red explosive is examined. The red explosive belongs to the most sensitive mixtures in the field of fireworks. Nos. 6, 7, 8 or 10, which contains metal powder, magnesium or aluminum, is more sensitive than the red explosive to the shock. With No. 1, No. 5 or No. 9 the sensitivity is thought to be roughly the same as that of the red explosive. These results are very surprising. However, even the red explosive, which has the highest shock sensitivity of other firework mixtures, does not perfectly ignite by the shock of 1.82 kg ball from 1 meter when it is placed on an anvil star. On a steel plate it ignites by the same ball from only 0.18 meters. The anvil star corresponds to the base part under the burning layer of each sample star. Therefore the buffer effect of the anvil star as well as the base part of the burning consolidated mixture against a shock is fairly large.

Before discussing the results in Table 4 of the small rocket burning test, some special patterns of burning in the open air must be considered.[4] For example, when mixtures ($KClO_3$ + S) and ($KClO_3$ + P) are mixed together into one mixture gradually changing the ratio, we obtain a series of compositions which change their shock sensitivity from low to high. The reaction pattern is “burning → explosion” or “burning → oscillatory burning → explosion” as the sensitivity of the compositions increases from low to high. With another type of mixtures, (Mg + $Sr(NO_3)_2$) and (Mg + NH_4ClO_4), the pattern is “burning → irregular burning → burning of another type”. Namely, middle reactions occur between both end reactions, “burning →→ explosion” or “burning →→ burning of another type”. These results come from the “dark reaction". The dark reaction means a precedent reaction where only easily activated component materials react to each other, leaving others in the burning layer of a consolidated mixture. The latter are activated by the precedent reaction and react with some delay.

The results in Table 4 might be produced by the dark reaction, because there are many middle reactions between the low and high pressures due to the increase of the values of *Ab/At*. It means that, when the burning pressure increases, the part which is highly activated reacts faster than the other. It is seen with remainders of burning through a microscope: many small craters or pits about 0.1 mm in diameter are found on the burnt surface and these may denote the places where the points of the dark reaction were proceeding.

The burning patterns in Table 4 are very different from each other and the surface explosion occurs only with the propellant type A, B and C in the *Ab/At* range from 79 to 178, and not with other types. (It must be noted that E: (NH_4ClO_4) smoothly burnt in a relatively wide range of *Ab/At*.) In this case, a precedent reaction activated the left components not so strong and the reaction did not proceed so deep from the original surface. This is a reverse effect with the propellant B which easily detonated in the range of *Ab/At* from 100 to 178.

The important result obtained by the small rocket burning test is that there arises a concept of "pressure sensitivity" other than the shock or friction sensitivity of mixtures. It is difficult to make mixtures explode only by pressing at normal temperatures. I only experienced it in the past when pressing the most sensitive mixture, potassium chlorate, red phosphorus and sulfur into a small paper tube using a device. The high pressure sensitivity is characterized by an explosion at a low value of *Ab/At* as it is with the propellant type B. The reverse is applied.

Other important point in this paper lies in that the sensitivity of burning surface layer of ordinary consolidated mixtures is very high like that of red explosive as formerly discussed. When a fire breaks out with some consolidated mixtures in a large scale, it is very dangerous to cause a great catastrophe due to some light shock.

I heard before the war a cannon was broken when using a propellant of short tubular grains, and after the accident it was replaced by that of long tubular grains to cause no accident, although the cause of the accident was not clear. The propellant contained nitroglycerin. At present I suppose that the cause of the accident came from the collision of high frequency among the burning propellant grains. It was wise to minimize the frequency of the collision of the burning grains, which might have a high shock sensitivity, not to cause a detonation.

Conclusion

(1) The shock sensitivity of the burning layer of various consolidated mixtures was examined by dropping an iron ball from a height of one meter onto the burning surface of a sample star. The surface explosion easily occurred. The sensitivity of the burning layer of mixtures used was generally higher than that of the red explosive which is thought to be the most sensitive in the firework field.

(2) The base part under the burning layer played a role of a fairly large buffer against the shock to decrease the sensitivity of the burning surface.

(3) Six types of propellant compositions were formed into a small tubular form and were burnt in small rocket engines. The burning patterns of the propellants were different from each other. The surface explosion occurred only with compositions of the propellant which contained potassium chlorate or potassium perchlorate, and not with ones which contained ammonium perchlorate.

(4) From a microscopic investigation of the surface of the remainder of propellant at the surface explosion in the small rocket engine, it is thought the surface explosion occurred due to a dark reaction of the surface, considering other phenomena, oscillatory or irregular burning, must come also from a dark reaction.

(5) From the test of the small rocket engines changing the values of *Ab/At*, a concept of "pressure sensitivity" arose. The sensitivity is high when a consolidated mixture explodes at a

small value of *Ab/At* and the reverse is also applied.

(6) With a Black Powder type mixture, the surface explosion did not occur.

(7) The surface explosion of consolidated mixtures may easily proceed to detonation when the pressure sensitivity is high.

References

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Stabilizing Firework Compositions
I. Minimum Solubility Law to Foresee the Degeneration
II. A New Chemical Method of Magnesium Coating

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ABSTRACT

These studies concern two important problems at present: one is how to select the component materials of a mixture not to cause degeneration, and another is to find a more effective method of magnesium coating than those at present.

A firework mixture generally consists of several solid materials which are closely in contact with each other. The state is not so much natural as artificial. Therefore, the mixture often causes chemical degeneration to remove into a more stable state which is opposite to the purpose. The direction of the change has been unknown without experiences. It has been a great difficulty on selecting materials. I have found a rule to foresee the direction: the component materials in a mixture gradually decompose with each other to create the most water insoluble material. This tendency should be called the "minimum solubility law". A table was prepared to foresee the direction of the degeneration reactions arranging materials in the order of their solubilities.

When a magnesium flake is soaked in a solution of dichromate and sulfate, the flake is gradually coated with a thin black film. It may be CrO_2 *and have a high corrosion resistance. The effect was tested with several dichromates and sulfates against mainly ammonium perchlorate using magnesium ribbon and powder. In addition an effect of guanidine nitrate on the coating was observed because it gave a good result of corrosion resistance when it was used as a blinker (strobes) in the past.*

1. Introduction

A firework composition generally consists of several materials, oxidizer, fuel, color producing agent, etc. The state of the mixture is not natural, but artificial. The materials are closely in contact with each other. Therefore, the mixture very often gradually degenerates chemically or sometimes physically to a more stable state. It causes many troubles, moisture absorption, no ignition, low light intensity, spontaneous ignition, etc.

The most important problems at present in the firework field to avoid the degeneration of mixture may be how to select the materials and how to protect metal powders especially magnesium from corrosion.

With the former we could have no reliable evidence without experiences in the past. However, with individual experience we cannot foresee the general rule. For example, R. Lancaster wrote "Never mix chlorates with ammonium salts".[1] On the other hand, in the German regulation we find that a mixture of chlorate and ammonium salt is forbidden, however, that of chlorate and ammonium chloride is allowed.[2] Another example is that: nitrate with ammonium salt is generally avoided due to producing a hygroscopic substance, but barium nitrate with ammonium perchlorate can be used with no hygroscopic troubles.[3] This paper will solve such contradictions and give us a general rule on the selection of the materials.

With the latter, many methods of physical or chemical coating are already presented.[4] However, it has been difficult to find the method to protect magnesium from corrosion intensive ammonium perchlorate which is important to make blinkers (strobes).

This paper suggests a new chemical coating method which may be more useful than those at present.

2. The Minimum Solubility Law

2.1 General Principles and Applications

The chemistry originally developed from a dilute solution of some substances in water or from vapor phase. However, our firework mixtures are in solid phase. The degeneration reaction occurs from a solid to solid among the component materials. From our experiences in almost all cases, we know the degeneration of such mixtures occurs from absorption of moisture in the air. Therefore, the state of our mixtures should be thought to be a highly concentrated solution of materials in water, where only the minimum amount of moveable ions of the materials will exist.

A traditional example of producing a precipitate in a dilute solution at 30 °C is shown with the reaction of silver nitrate with sodium chloride:

$$\underset{216}{AgNO_3} + \underset{36.1}{NaCl} \rightarrow \underset{0.00024}{AgCl\downarrow} + \underset{96.0}{NaNO_3}$$

where the figures under symbols show the solubility of each material in 100 grams of water at 30 °C, the horizontal arrow shows the direction of proceeding of the reaction, and the downward arrow shows the formation of precipitate. These expressions are used hereafter. When the data of solubility of individual substance are not available at 30 °C, those of near 30 °C are used.

As it is seen in above formula, the reaction proceeds from the left side to the right. In a dilute solution of materials, it is a very common rule of a double decomposition (i.e., the reaction in a dilute solution proceeds to form a substance which has the minimum solubility of all). The firework mixtures, especially when they are consolidated, are not a dilute solution, but a solid. However, as described above, they may be thought to be a highly concentrated solution in water because they absorb more or less a very small amount of moisture. Therefore, even in the consolidated state the reaction may proceeds in the direction to produce a substance of minimum solubility as it is with the precipitate formation in the dilute solution. However, it takes a long time, several days, months or years because of few active ions. In this paper the author calls this reaction rule as the “minimum solubility law”.

A table was prepared to confirm above theory or to foresee the directions of degeneration reactions (Table 1). In the table, materials are arranged in the order of their solubilities.

A few examples of foreseeing the degeneration reactions are presented from Table 1.

Notes for Table 1:

a) The arrangement in Table 1 is as follows:

<table>
<tr><td colspan="20">Material
Order Number of Solubility</td></tr>
<tr><td rowspan="11">Material</td><td rowspan="11">Solubility in 100 g of Water</td><td rowspan="11">Order Number of Solubility</td><td>–</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td rowspan="11">Order number of Solubility</td><td rowspan="11">Nateruak</td></tr>
<tr><td>e</td><td>–</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td></tr>
<tr><td>e</td><td>e</td><td>–</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td></tr>
<tr><td colspan="15">Direction of Degeneration</td></tr>
<tr><td>e</td><td>e</td><td>e</td><td colspan="9">(Stability)</td><td>e</td><td>e</td><td>e</td></tr>
<tr><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td></tr>
<tr><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td></tr>
<tr><td colspan="15"></td></tr>
<tr><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>–</td><td>e</td><td>e</td></tr>
<tr><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>–</td><td>e</td></tr>
<tr><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>e</td><td>–</td></tr>
</table>

b) Symbols for materials are denoted in combination of cation with anion:

Cation	1: K–	Anion:	A: $–NO_3$	H: $=Cr_2O_7$
	2: Na–		B: $–ClO_3$	I: –Cl
	3: Sr=		C: $–ClO_4$	J: $=C_2O_4$
	4: Ba=		D: $=CO_3$	
	5: Ca=		F: $=SO_4$	
	6: NH_4–		G: $=CrO_4$	

For example, potassium nitrate is denoted by 1A which means KNO_3 or Strontium carbonate by 3D which means $SrCO_3$.

c) General symbols:

S: no reaction, stable,
s: stable due to common ions between two materials,
x: degenerates, unstable
a: unstable when alkaline,
?: uncertain due to no data of solubility,
*: no data when acid is formed, but certain with experiment.

d) The data of solubility were taken from reference 5. These are the values at or near 30 ºC.

The reaction of potassium chlorate (1B) and ammonium perchlorate (6C) is found at the crossing point of the horizontal line of 1B with the vertical line of 6C as a symbol x which denotes unstab1e. This reaction is expressed as:

$$\begin{array}{ccc} KClO_3 & + & NH_4ClO_4 \rightarrow \\ 10.1 & & 29.9 \end{array}$$

$$\begin{array}{ccc} KClO_4\downarrow & + & NH_4ClO_3 \\ 2.6 & & 53.4 \end{array} \qquad (1)$$

In the same way with potassium chlorate (1B) and ammonium chloride (6I) the crossing point denotes stable with a symbol S:

$$\begin{array}{ccc} KClO_3\downarrow & + & NH_4Cl \leftarrow \\ 10.1 & & 41.4 \end{array}$$

$$\begin{array}{ccc} KCl & + & NH_4ClO_3 \\ 37.2 & & 53.4 \end{array} \qquad (2)$$

Table 1. Table for Foreseeing Degeneration Reaction at 30 ºC with Two Materials in a Solid Mixture Based on the Minimum Solubility Law.

		No.	4F 1	4G 2	5J 3	3D 4	3F 5	4D 6	3J 7	4J 8	5D 9	3G 10	5F 11	1C 12	2J 13	1B 14	4A 15	1F 16	5G 17	1H 18	6C 19	2I 20	1I 21	4I 22	6G 23	1J 24
4F	0.00029	1	–	s	S	S	s	s	S	s	S	S	s	S	S	S	s	s	S	S*	S	S	S	s	S	S
4G	0.00046	2	s	–	S	S	x	s	S	s	S	s	x	S	x	S	s	x	s	S*	S	S	S	s	s	S
5J	0.00073	3	S	S	–	S	S	S	s	s	s	S	s	S	s	S	S	S	s	S	S	S	S	S	S	s
3D	0.00090	4	S	S	S	–	s	s	s	S	s	s	S	S	S	S	S	S	S	S	S	S	S	S	S	S
3F	0.00138	5	s	x	S	s	–	x	s	S	x	s	S	S	S	S	x	s	S	S	S	S	S	x	S	S
4D	0.0034	6	s	s	S	s	x	–	x	s	s	x	x	S	S	S	s	x	x	x	S	S	S	s	S	S
3J	0.00461	7	S	S	s	s	s	s	–	s	x	s	x	S	s	S	S	x	x	?	S	S	S	S	S	s
4J	0.0140	8	s	s	s	S	S	s	s	–	x	x	x	S	s	S	s	x	x	?	S	S	S	s	x	s
5D	0.072	9	S	S	s	s	x	s	x	x	–	x	s	S	x	S	x	S	s	S	S	S	S	x	S	x
3G	0.096	10	S	s	S	s	s	x	s	x	x	–	x	S	x	S	x	x	s	?	S	S	S	x	s	x
5F	0.209	11	s	x	s	S	S	x	x	x	s	x	–	S	x	S	x	s	s	S	S	S	S	x	S	x
1C	2.6	12	S	S	S	S	S	S	S	S	S	S	S	–	S	s	S	s	S	s	s	S	s	S	S	s
2J	3.8	13	S	x	s	S	S	S	s	s	x	x	x	S	–	S	x	S	x	S	S	s	S	x	S	s
1B	10.1	14	S	S	S	S	S	S	S	S	S	S	S	s	S	–	S	s	S	s	x	S	s	S	S	s
4A	11.4	15	s	s	S	S	x	s	S	s	x	x	x	S	x	S	–	x	x	x	S	S	S	s	x	x
1F	13.0	16	s	x	S	S	s	x	x	x	S	x	s	s	S	s	x	–	x	s	x	S	s	x	S	s
5G	16.1	17	S	s	s	S	S	x	x	x	s	s	s	S	x	S	x	x	–	S	S	S	S	x	s	x
1H	19.1	18	S*	S*	S	S	S	x	?	?	S	?	S	s	S	s	x	s	S	–	S	S	s	?	S	s
6C	29.9	19	S	S	S	S	S	S	S	S	S	S	S	s	S	x	S	x	S	S	–	S	x	S	s	x
2I	36.1	20	S	S	S	S	S	S	S	S	S	S	S	S	s	S	S	S	S	S	S	–	s	s	S	x
1I	37.1	21	S	S	S	S	S	S	S	S	S	S	S	s	S	s	S	s	S	s	x	s	–	s	S	s
4I	38.3	22	s	s	S	S	x	s	S	s	x	x	x	S	x	S	s	x	x	?	S	s	s	–	x	x
6G	39.9	23	S	s	S	S	S	S	S	x	S	s	S	S	S	S	x	S	s	S	s	S	S	x	–	S
1J	40.1	24	S	S	s	S	S	S	s	s	x	x	x	s	s	s	x	s	x	s	x	x	s	x	S	–
2F	41.2	25	s	x	S	S	s	x	x	x	S	x	s	S	s	S	x	s	x	x	S	s	x	x	S	x
6I	41.4	26	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	s	s	s	s	s	x
4B	41.7	27	s	s	S	S	x	s	S	s	x	x	x	S	x	s	s	x	x	?	S	S	x	s	x	x
2D	45.3	28	S	S	S	s	x	s	x	x	s	x	x	S	s	S	x	S	x	S	S	s	x	x	S	x
1A	45.6	29	S	S	S	S	S	S	S	S	S	S	S	s	S	s	s	s	S	s	x	S	s	x	S	s
6H	46.5	30	?	?	S	?	?	?	?	?	S	?	S	S	S	S	?	S	S	s	s	S	x	?	s	x
6B	53.4	31	S	S	S	S	S	S	S	S	S	S	x	S	S	s	S	x	S	x	s	S	x	x	s	x
6D	55.8	32	S	S	S	s	x	s	x	x	s	x	x	S	x	S	x	S	x	S	s	S	S	x	s	S
3I	58.5	33	S	S	S	s	s	x	s	x	x	s	x	S	x	S	S	x	x	?	S	s	s	s	x	x
6J	59.0	34	S	S	s	S	S	S	s	s	x	x	x	S	s	S	x	S	x	S	s	x	S	x	s	s
1G	66.1	35	S	s	S	S	S	x	S	x	S	s	S	s	S	s	x	s	s	s	S	S	s	x	s	s
6F	77.8	36	s	x	S	S	s	x	x	x	S	x	s	S	S	S	x	s	x	x	s	S	x	x	s	x
5H	83.0	37	?	?	s	?	?	?	?	?	s	?	s	S	x	S	?	x	s	s	S	S	x	?	x	x
2G	88.0	38	S	s	S	S	S	x	S	x	S	s	S	S	s	S	x	S	s	S	S	s	x	x	s	x
3A	88.7	39	S	S	S	s	s	x	s	x	x	s	x	S	x	S	s	x	x	ax	S	S	S	x	x	x
2A	96.0	40	S	S	S	S	S	x	S	S	S	S	S	S	s	S	s	x	S	S	S	s	x	x	S	x
5I	100	41	S	S	s	S	S	S	x	x	s	S	s	S	x	S	S	x	s	S	S	s	s	s	S	x
2B	105	42	S	S	S	S	S	S	S	S	S	S	S	S	s	s	S	x	S	x	S	s	x	x	S	x
1D	114	43	S	S	S	s	x	s	x	x	s	x	x	s	S	s	x	s	x	s	x	S	s	x	S	s
5A	153	44	S	S	s	S	S	S	x	x	s	S	s	S	x	S	s	x	s	S	S	S	S	x	x	x
3B	178	45	S	S	S	s	s	x	s	x	x	s	x	S	x	s	S	x	x	?	S	S	x	S	x	x
2H	192	46	?	?	S	?	?	?	?	?	S	?	S	S	s	S	?	S	S	s	S	s	x	?	S	x
5B	194	47	S	S	s	S	S	S	x	x	s	S	s	S	x	s	S	x	s	x	S	S	x	S	x	x
5C	202	48	S	S	s	S	S	S	x	x	s	S	s	s	x	x	S	x	s	x	s	S	x	S	x	x
2C	219	49	S	S	S	S	S	S	S	S	S	S	S	s	s	x	S	x	S	x	s	s	x	x	x	x
6A	238	50	S	S	S	S	S	S	S	S	S	S	S	S	S	S	s	S	S	S	s	S	S	x	s	S
4C	320	51	s	s	S	S	x	s	S	s	x	x	x	s	x	x	s	x	x	?	s	S	x	s	x	x
3C	327	52	S	S	S	s	s	x	s	S	x	s	x	s	x	x	S	x	x	?	s	S	x	S	x	x

Table 1. Table for Foreseeing Degeneration Reaction at 30 ºC with Two Materials in a Solid Mixture Based on the Minimum Solubility Law. (Continued)

2F	6I	4B	2D	1A	6H	6B	6D	3I	6J	1G	6F	5H	2G	3A	2A	5I	2B	1D	5A	3B	2H	5B	5C	2C	6A	4C	3C		
25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	52	52	No.	4F
s	S	s	S	S	?	S	S	S	S	S	s	?	S	S	S	S	S	S	S	S	?	S	S	S	S	s	S	1	4F
x	S	s	S	S	?	S	S	S	S	s	x	?	s	S	S	S	S	S	S	S	?	S	S	S	S	s	S	2	4G
S	S	S	S	S	S	S	S	S	s	S	S	s	S	S	S	s	S	S	s	S	S	s	s	S	S	S	S	3	5J
S	S	S	s	S	?	S	s	s	S	S	S	?	S	s	S	S	S	s	S	s	?	S	S	S	S	S	s	4	3D
s	S	x	x	S	?	S	x	s	S	S	s	?	S	s	S	S	S	x	S	s	?	S	S	S	S	x	s	5	3F
x	S	s	s	S	?	S	s	x	S	x	x	?	x	x	x	S	S	s	S	x	?	S	S	S	S	s	x	6	4D
x	S	S	x	S	?	S	x	S	s	S	x	?	S	s	S	x	S	x	x	S	?	x	x	S	S	S	s	7	3J
x	S	s	x	S	?	S	x	x	s	x	x	?	x	x	S	x	S	x	x	x	?	x	x	S	S	s	S	8	4J
S	S	x	s	S	S	S	s	x	x	S	S	s	S	x	S	s	S	s	s	x	S	s	s	S	S	x	x	9	5D
x	S	x	x	S	?	S	x	s	x	s	x	?	s	s	S	S	S	x	S	s	?	S	S	S	S	x	s	10	3G
s	S	x	x	S	S	x	x	x	x	S	s	s	S	x	S	s	S	x	s	x	S	s	s	S	S	x	x	11	5F
S	S	S	S	s	S	S	S	S	S	s	S	S	S	S	S	S	S	s	S	S	S	S	s	s	S	s	s	12	1C
s	S	x	s	S	S	S	x	x	s	S	S	x	s	x	s	x	s	S	x	x	s	x	x	s	S	x	x	13	2J
S	S	s	S	s	S	s	S	S	S	s	S	S	S	S	S	S	s	s	S	s	S	s	x	x	S	x	x	14	1B
x	S	s	x	s	?	S	x	S	x	x	x	?	x	s	s	S	S	x	s	S	?	S	S	S	s	s	S	15	4A
s	S	x	S	s	S	x	S	x	S	s	s	x	S	x	x	x	x	s	x	x	S	x	x	x	S	x	x	16	1F
x	S	x	x	S	S	S	x	x	x	s	x	s	s	x	S	s	S	x	s	x	S	s	s	S	S	x	x	17	5G
x	S	?	S	s	s	x	S	?	S	s	x	s	S	ax	S	S	x	s	S	?	s	x	x	x	S	?	?	18	1H
S	s	S	S	x	s	s	s	S	s	S	s	S	S	S	S	S	S	x	S	S	S	S	s	s	s	s	s	19	6C
s	s	S	s	S	S	S	S	s	x	S	S	S	s	S	s	s	s	S	S	S	s	S	S	s	S	S	S	20	2I
x	s	x	x	s	x	x	S	s	S	s	x	x	x	S	x	s	x	s	S	x	x	x	x	x	S	x	x	21	1I
x	s	s	x	x	?	x	x	s	x	x	x	?	x	x	x	s	x	x	x	S	?	S	S	x	x	s	S	22	4I
S	s	x	S	S	s	s	s	x	s	s	s	x	s	x	S	S	S	S	x	x	S	x	x	x	s	x	x	23	6G
x	x	x	x	s	x	x	S	x	s	s	x	x	x	x	x	x	x	s	x	x	x	x	x	x	S	x	x	24	1J
–	x	x	s	x	S	S	S	x	x	x	x	x	s	x	s	x	s	x	x	x	s	x	x	s	S	x	x	25	2F
x	–	x	x	x	s	s	s	s	s	x	s	S	x	S	x	s	x	x	S	S	x	S	x	x	s	x	x	26	6I
x	x	–	x	x	?	s	s	x	x	x	x	?	x	x	x	x	s	x	x	s	?	s	S	S	x	s	S	27	4B
s	x	x	–	S	S	S	s	x	x	S	x	x	s	x	s	x	s	s	x	x	s	x	x	s	S	x	x	28	2D
x	x	x	S	–	x	x	S	x	x	s	x	x	S	s	s	S	S	s	s	x	x	x	x	x	s	x	x	29	1A
S	s	?	S	x	–	s	s	?	s	x	s	s	x	?	S	x	S	S	S	?	s	S	x	x	s	?	?	30	6H
S	s	s	S	x	s	–	s	x	s	x	s	x	x	S	s	x	s	x	S	s	x	s	x	x	s	x	x	31	6B
S	s	s	s	S	s	s	–	x	s	x	s	x	x	x	x	x	x	s	x	x	x	x	x	x	s	x	x	32	6D
x	s	x	x	x	?	x	x	–	x	x	x	?	x	s	x	s	x	x	S	s	?	S	S	x	x	x	s	33	3I
x	s	x	x	x	s	s	s	x	–	x	s	x	x	x	x	x	x	x	x	x	x	x	x	x	s	x	x	34	6J
x	x	x	S	s	x	x	x	x	x	–	x	x	s	x	x	x	x	s	x	x	x	x	x	x	x	x	x	35	1G
x	s	x	x	x	s	s	s	x	s	x	–	x	x	x	x	x	x	x	x	x	x	x	x	x	s	x	x	36	6F
x	S	?	x	x	s	x	x	?	x	x	x	–	x	?	S	s	S	x	s	?	s	s	s	S	x	?	?	37	5H
s	x	x	s	S	x	x	x	x	x	s	x	x	–	x	s	x	s	x	S	x	s	x	x	s	x	x	x	38	2G
x	S	x	x	s	?	S	x	s	x	x	x	?	x	–	s	x	S	x	s	s	?	S	S	S	s	x	s	39	3A
s	x	x	s	s	S	S	x	x	x	x	x	S	s	s	–	x	s	x	s	x	s	S	S	s	s	x	x	40	2A
x	s	x	x	S	x	x	x	s	x	x	x	s	x	x	x	–	x	x	s	x	x	s	s	x	x	x	x	41	5I
s	x	s	s	S	S	s	x	x	x	x	x	S	s	S	s	x	–	x	x	s	s	s	S	s	x	x	S	42	2B
x	x	x	s	s	S	x	s	x	x	s	x	x	x	x	x	x	x	–	x	x	x	x	x	x	x	x	x	43	1D
x	S	x	x	s	S	s	x	S	x	x	x	s	S	s	s	s	x	x	–	x	x	s	s	x	s	x	x	44	5A
x	S	s	x	x	?	s	x	s	x	x	x	?	x	s	x	x	s	x	x	–	?	s	S	x	x	x	s	45	3B
s	x	?	s	x	s	x	x	?	x	x	x	s	s	?	s	x	s	x	x	?	–	x	x	s	x	?	?	46	2H
x	S	s	x	x	S	s	x	S	x	x	x	s	x	S	S	s	s	x	s	s	x	–	s	x	x	x	x	47	5B
x	x	S	x	x	x	x	x	S	x	x	x	s	x	S	S	s	S	x	s	S	x	s	–	s	x	s	s	48	5C
s	x	S	s	x	x	x	x	x	x	x	x	S	s	S	s	x	s	x	x	x	s	x	s	–	x	s	s	49	2C
S	s	x	S	s	s	s	s	x	s	x	s	x	x	s	s	x	x	x	s	x	x	x	x	x	–	x	x	50	6A
x	x	s	x	x	?	x	x	x	x	x	x	?	x	x	x	x	x	x	x	x	?	x	s	s	x	–	s	51	4C
x	x	S	x	x	?	x	x	s	x	x	x	?	x	s	x	x	S	x	x	s	?	x	s	s	x	s	–	52	3C

The reaction (1) proceeds toward the right side because the $KClO_4$ has the minimum solubility of all. This reaction creates very dangerous ammonium chlorate which easily causes a spontaneous decomposition. On the other hand, the reaction (2) causes no reaction because $KClO_3$ at the left side has the minimum solubility of all. These are to explain the German regulation forbids the mixture of potassium chlorate and ammonium salts, but allows that of potassium chlorate and ammonium chloride.[2]

With the reactions of ammonium perchlorate and nitrates in the same way we find:

$$\begin{array}{llll} NH_4ClO_4 \ (6C) & + & KNO_3 \ (1A) & \rightarrow \\ 29.9 \quad 45.6 & & & \end{array}$$

$$\begin{array}{llll} NH_4NO_3 \ (6A) & + & KClO_4 (1C)\downarrow & \\ 238 & & 2.6 & (3) \end{array}$$

$$\begin{array}{llll} 2\ NH_4ClO_4 \ (6C) & + & Ba(NO_3)_2 \ (4A)\downarrow\leftarrow & \\ 29.9 & & 11.4 & \end{array}$$

$$\begin{array}{llll} 2\ NH_4NO_3 \ (6A) & + & Ba(ClO_4)_2 \ (4C) & \\ 238 & & 320 & (4) \end{array}$$

(3) and (4) explain our experiences: when ammonium perchlorate is mixed with potassium nitrate, the mixture gradually absorbs moisture in the air to become muddy due to the high hygroscopic nature of the ammonium nitrate. On the other hand, when ammonium perchlorate is mixed with barium nitrate, no reaction occurs. The reason is that the reaction (3) proceeds to the right due to the formation of $KClO_4$ which has the minimum solubility, while the latter (4) stops in the left due to the minimum solubility of $Ba(NO_3)_2$.

2.2. Dichromate Reactions

A special attention should be paid with reactions of dichromate to apply the minimum solubility law. Dichromate salts are important to protect metals, especially magnesium, from corrosion. With ammonium perchlorate the reaction proceeds as follows:

$$\begin{array}{llll} K_2Cr_2O_7 & + & 2\ NH_4ClO_4 & \rightarrow \\ 19.1 & & 29.9 & \end{array}$$

$$\begin{array}{llll} 2\ KClO_4\downarrow & + & (NH_4)_2Cr_2O_4 & (5) \\ 2.6 & & 46.5 & \end{array}$$

In this case the reaction proceeds in the same way as the reaction (1). This is an ordinary reaction which follows the minimum solubility law. (In this reaction the volume of the right side mixture increases five percents from the left. Therefore, it is better to use the ammonium dichromate in place of the potassium dichromate to avoid cracking of stars during the store.) However, when using dichromates, they often create acid. The values of solubility of materials in acid are not always clear. In such cases, the direction of degeneration reaction must be experimentally confirmed. Examples are shown as follows (the solubilities noted are the values in water):

$K_2Cr_2O_7$	+	$Sr(NO_3)_2$	+	H_2O	$\rightarrow$	K_2CrO_4	+	$SrCrO_4\downarrow$	+	$2\ HNO_3$	(6)
18.1		88.7				66.1		0.096			
$K_2Cr_2O_7$	+	$SrSO_4\downarrow$	+	H_2O	$\leftarrow$	K_2CrO_4	+	$SrCrO_4$	+	H_2SO_4	(7)
18.1		0.00138				66.1		0.096			
$K_2Cr_2O_7$	+	$SrCO_3\downarrow$	+	H_2O	$\leftarrow$	K_2CrO_4	+	$SrCrO_4$	+	H_2CO_3	(8)
18.1		0.00090				66.1		0.096			
$K_2Cr_2O_7$	+	$Ba(NO_3)_2$	+	H_2O	$\rightarrow$	K_2CrO_4	+	$BaCrO_4\downarrow$	+	$2\ HNO_3$	(9)
18.1		11.5				66.1		0.00046			
K_2CrO_7	+	$BaSO_4\downarrow$	+	H_2O	$\leftarrow$	K_2CrO_4	+	$BaCrO_4$	+	H_2SO_4	(10)
18.1		0.0029				66.1		0.00046			
$K2CrO_7$	+	$BaCO_3$	+	H_2O	$\rightarrow$	K_2CrO_4	+	$BaCrO_4\downarrow$	+	H_2CO_3	(11)
18.1		+.0022				66.1		0.00046			

Of these reactions, (7), (8), (9) and (11) follow the minimum solubility law in water, (6) follows the law when the mixture is alkaline, and (10) does not follow experimentally.

3. A New Chemical Method of Magnesium Coating

3.1. Preliminary Experiment with Potassium Dichromate

The author tested with various consolidated mixtures to see the effect of potassium dichromate on magnesium from 1980 to 1987. The sample compositions are shown in Table 2.

Table 2. Sample Compositions for Preliminary Test.

(1) Base composition	A	B	C	D	E	F	G	H	I
Mg	30%	20%	30%	30%	30%	40%	23%	20%	–%
Mg–Al(50/50)	—	—	—	—	—	—	—	—	25
NH_4ClO_4	50	60	60	60	60	50	60	60	60
$SrSO_4$	20	20	—	—	—	—	—	—	—
$CaSO_4$	—	—	10	—	—	—	—	—	—
$NaNO_3$	—	—	—	10	—	—	—	—	—
Na_2SO_4	—	—	—	—	10	10	—	—	—
$BaSO_4$	—	—	—	—	—	—	17	—	—
$Ba(NO_3)_2$	—	—	—	—	—	—	—	20	15
(2) Sample composition	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
Base composition	A	B	C	D	E	F	G	H	I
$K_2Cr_2O_7$ (add'l. %)	5	5	5	5	5	5	5	5	5
(3) Sample composition	No. 10	No. 11	No. 12	No. 13	No. 14	No. 15	No. 16	No. 17	No. 18
Base composition	A	B	C	D	E	F	G	H	I
$K_2Cr_2O_7$ (add'l. %)	5	5	5	5	5	5	5	5	5
Guanidine nitrate (add'l %) $C(NH)(NH)_2 \bullet HNO_3$	10	10	10	10	10	10	10	10	10

Note: 1. Magnesium powder passed 80 mesh, manufactured by Mitsuwa Kinzoku Co., Magnalium passed 100 mesh, manufactured by Tachikawa Yozai Co. These were coated with 5% potassium dichromate before the mixing.

2. Other chemicals were first class reagents except the guanidine nitrate.

3. Guanidine nitrate was used after recrystalization from the product by Chugoku-Kayaku Co.

100 grams of each mixture were consolidated with 10% nitrocellulose solution in acetone in a form of cut star of 8 mm cube.

The sample stars were placed naturally for years in a room of our laboratory without air conditioning. The results of degeneration are shown in Table 3 and Figure 1.

Table 3 The Results of Degeneration (After Seven Years and Ten Months).

Sample composition	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
Exterior view	f	c	w+c	g	g	g+c	g+f	w	g+c
Ignition	no	no	no	no	no	no	no	no	no
Sample Composition	**No. 10**	**No. 11**	**No. 12**	**No. 13**	**No. 14**	**No. 15**	**No. 16**	**No. 17**	**No. 18**
Exterior view	g	g	g	b	b	b	g	w+c	g
Ignition	i	i	i	no	i	i	i	no	no

Note: Symbols:

f:	a white substance oozed out of the surface to form white flecks,
c:	cracked,
w+c:	became white and cracked,
g:	became gray,
g+c:	became gray and cracked,
w:	became white,
g+f:	became gray and a white substance oozed out of the surface,
b:	became black,
i:	ignited with black match and blinked,
no:	no ignition with black match.

The initial view of all the stars was brownish gray. In spite of the long time store of about eight years, the compositions Nos. 10, 11, 12, 14, 15 and 16 were still vivid and others all died.

3.2. Experimental Research with the Foregoing Effect

In combination of Table 2 with Table 3, the difference between the vivid and died is that the compositions of the former contain some sulfate, while those of the latter no sulfate. Sulfates should be the most important material to avoid corrosion of magnesium.

The next important material should be guanidine nitrate because the sample compositions were not vivid without this material (see compositions Nos. 1–9).

Magnesium or some times magnalium, ammonium perchlorate and potassium dichromate were common to all compositions. To protect magnesium from corrosion, some dichromate is thought to be chemically the most effective from our experiences and ammonium perchlorate is the strongest enemy against magnesium when we plan firework compositions.

From above considerations, three materials, some sulfate, guanidine nitrate and some dichromate, in combination may be chemically the most effective for the magnesium coating. To make this point more clear, the following experiment was carried out.

Several pieces of magnesium ribbon for chemical use (0.2 mm thick and 3 mm wide) were soaked in saturated sulfate and ammonium dichromate solutions in water in test tubes and were observed. As the sulfates, K_2SO_4, Na_2SO_4, $(NH_4)_2SO_4$, $MgSO_4$ and $Al_2(SO_4)_3$ were used and as the dichromate $(NH_4)_2Cr_2O_7$ was used. At the beginning tiny bubbles were formed on the surface of the magnesium ribbon. Then the surface changed its color silver to brown and then black, and the generation of the bubble ceased. During the bubble generation the pieces of the ribbon rose to the surface of the solution. Therefore, it was stirred at intervals to sink them. The reaction took about 24 hours to complete perfectly the black film on the surface of the ribbon. Only the ammonium sulfate did not make a good film: it looked as if the film exfoliated in the solution during the reaction.

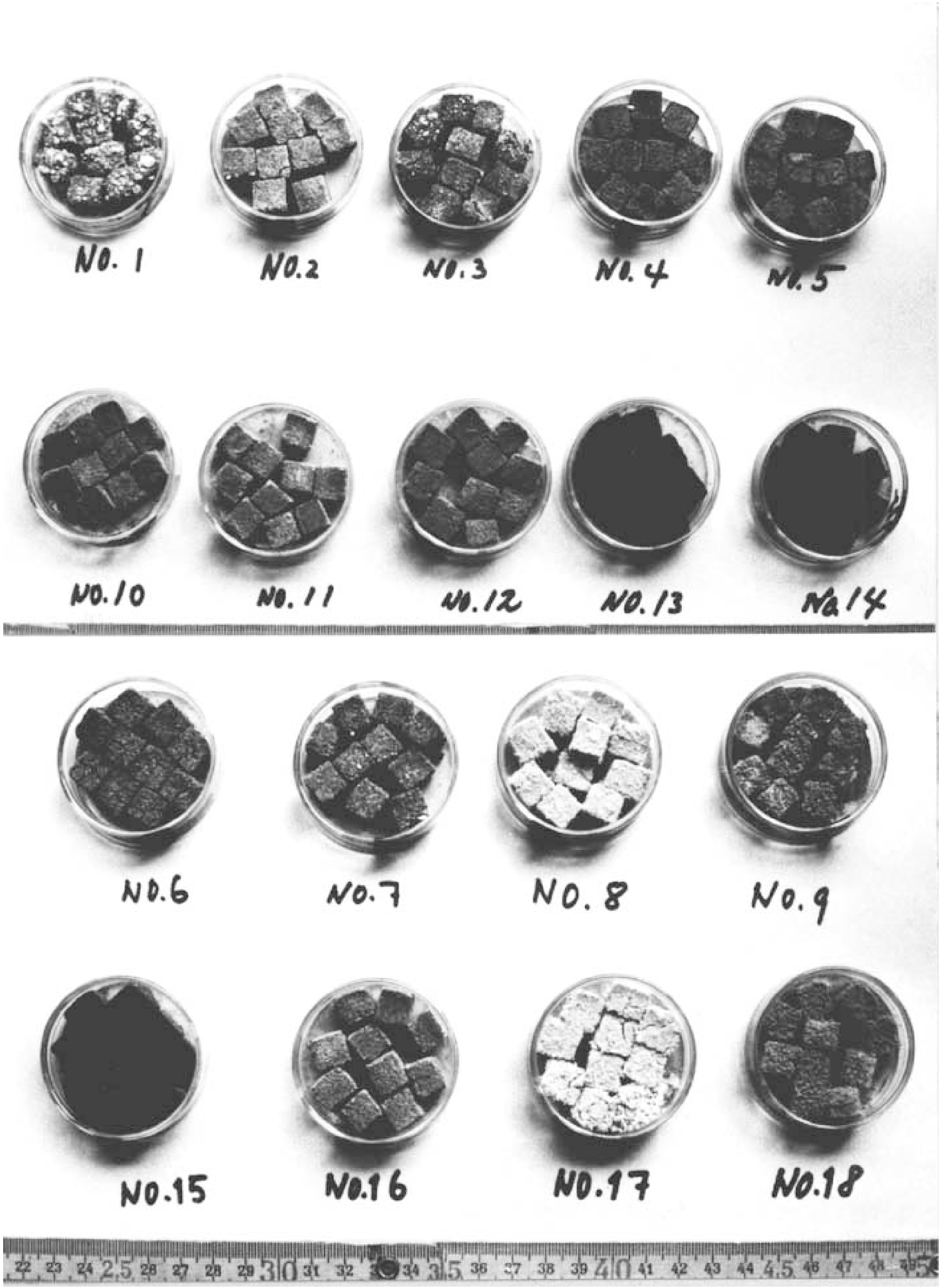


Figure 1. The appearance of sample stars after a long store of seven years and ten months.

Then a corrosion test was carried out with the magnesium ribbon pieces coated with the black film. They were soaked in a saturated ammonium perchlorate solution in water and left for hours. The pieces from potassium sulfate, sodium sulfate, magnesium sulfate and aluminum sulfate were not attacked by the solution after three and a half days except making few pinholes. Those from ammonium sulfate were fairly attacked and at last dissolved in the solution continually generating small bubbles. (Figure 2)

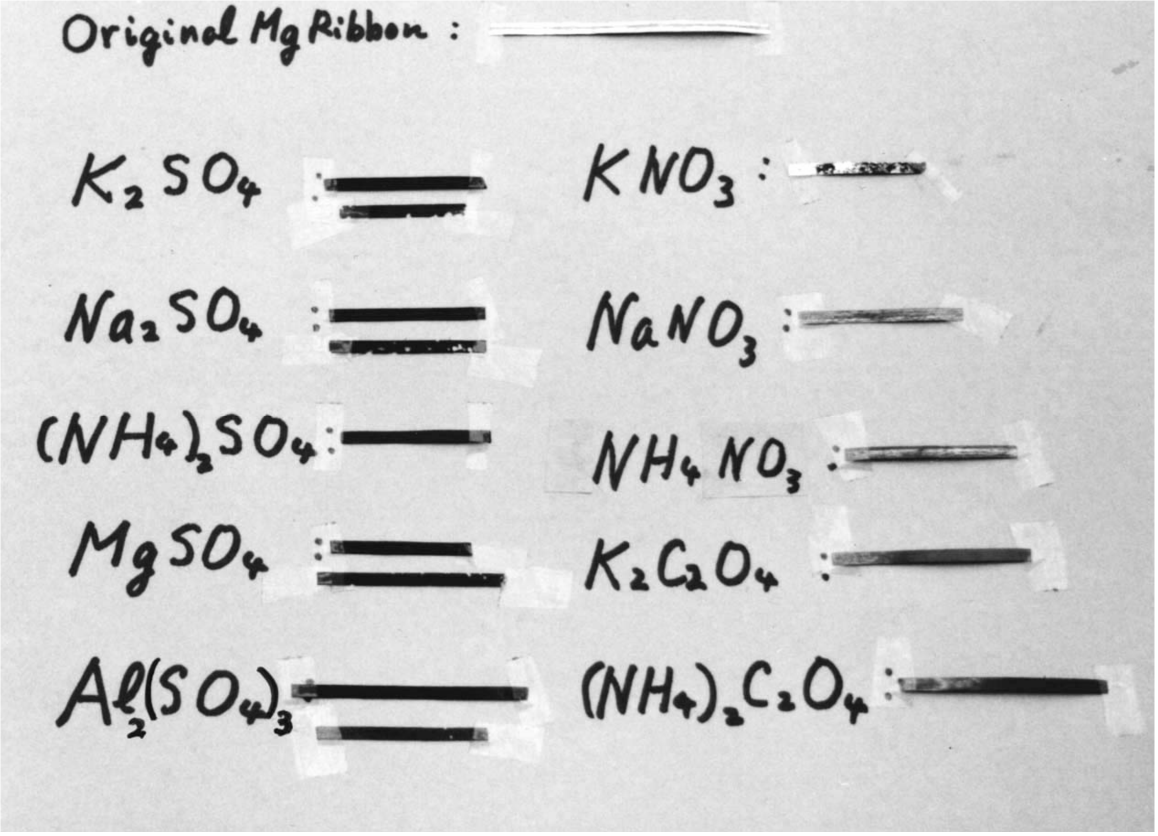


Figure 2. Results of chemical coating on magnesium ribbon pieces using saturated solution of sulfates, nitrates and oxalates with ammonium dichromate.

Note: For each sample, the upper piece is of no corrosion test, the lower passed corrosion test in a saturated solution of ammonium perchlorate in water, and shows few tiny pinholes. There are no lower samples with nitrates and oxalates because they are all dissolved at the corrosion test. The same is true for ammonium sulfate.

It is seen from the above experiment the black film is very effective to protect magnesium from corrosion caused by ammonium perchlorate. For comparison, with other materials, KNO_3, $NaNO_3$, NH_4NO_3, $K_2C_2O_4$ and $(NH_4)_2C_2O_4$, the same experiment as above was carried out. All of them did not give the black film, but only the oxalates gave a thin brown film. At the corrosion test the magnesium pieces after the soaking all dissolved in the ammonium perchlorate solution without resistance.

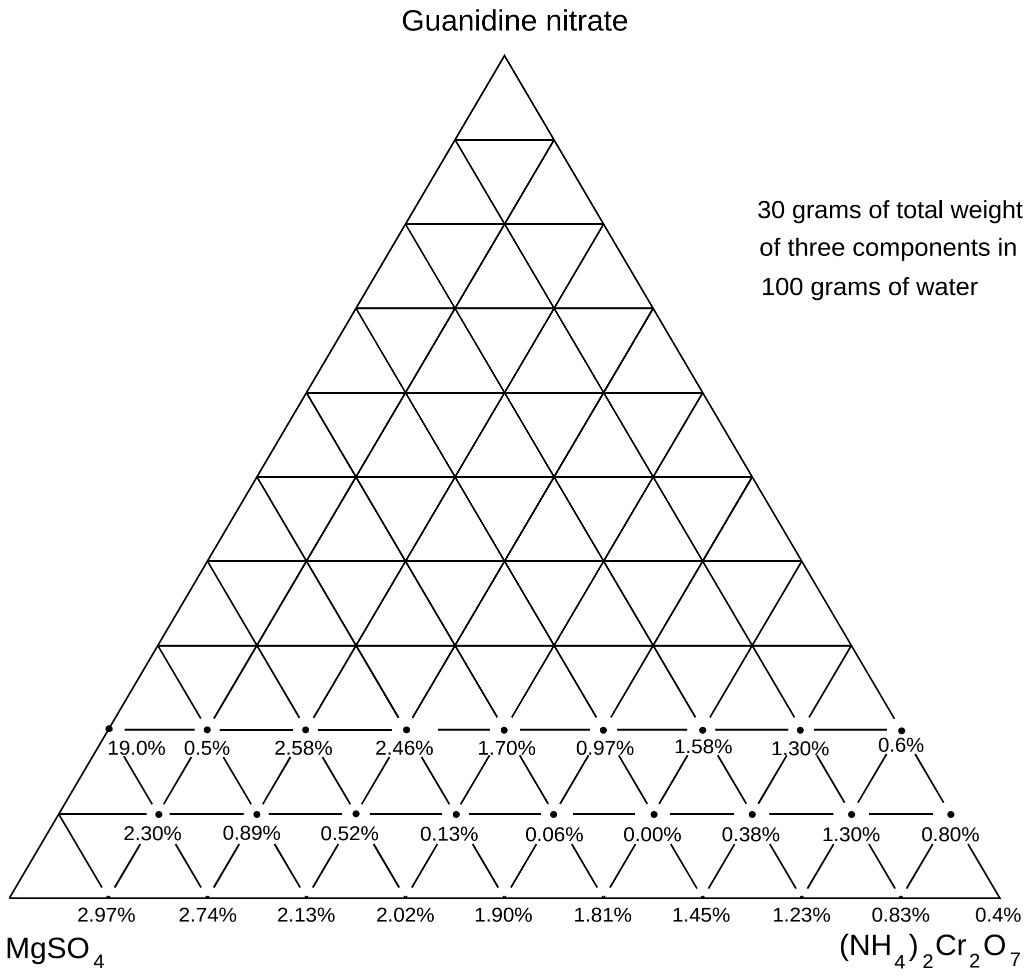
The principle of making the black film which is very corrosion resistant against ammonium perchlorate is thought to be as follows. The magnesium ribbon pieces in the sulfate solution generate hydrogen gas as tiny bubbles reacting with the sulfate very slowly. The values of pH of the solution were 3.5–4.0 which showed slight acidity at the test. Then the dichromate is reduced by the hydrogen to CrO_2 which forms the black film on the surface of the magnesium ribbon pieces. The reducing reaction of the nitrates or oxalates is very weak and they cannot form the black film in a short time. It is understood from the phenomenon that the ribbon pieces rose to the surface of the solution by the buoyancy of the hydrogen bubbles when using sulfates, but when the nitrates or oxalates were used, the phenomenon was not intensive, although the values of pH of the solution were the same as those of the former.

The black film is formed with only sulfate and dichromate. Therefore, it looks as if there were no use of guanidine nitrate. From the results in Table 3, however, this material plays an important role to give the corrosion resistance to the film, because the ignitions occurred only when the compositions contained guanidine nitrate (Table 2, 3, Nos. 10–12 and Nos. 14–16). Soaking tests of the magnesium ribbon in three component solutions of magnesium sulfate, ammonium dichromate and guanidine nitrate in various ratios (Figure 3) were carried out. (Magnesium sulfate was selected from other sulfates because it seemed as it was the most effective in forming the black film.) The figures in Figure 3 show the weight decrease of the sample pieces during the soaking in the solution for 28 hours. From this result it is thought that guanidine nitrate suppresses the reaction of magnesium. The effect is the largest when the value of the percentage of guanidine nitrate is 10% of all materials. The author observed that black film which was formed without such suppression caused exfoliation from the surface of the magnesium ribbon to a black powder, and at the corrosion test the ribbon pieces showed very poor effect.

The tests above described were practiced at room temperatures. On the other hand, several tests were carried out at 80 °C; however, the effects were not good.

From the results described above it is concluded that the reaction to form the black film on the magnesium surface must be slow at ordinary temperatures using a mixture of proper ratio of guanidine nitrate, some sulfate except ammonium sulfate, and some dichromate.

The results of this section will be reasonably connected with those of the foregoing experi-



30 grams of total weight
of three components in
100 grams of water

Figure 3. Weight decrease of magnesium ribbon pieces after soaking in guanidine nitrate, magnesium sulfate and ammonium dichromate solution in water for 28 hours.

ment in 3.1. In Figure 1 the stars without guanidine nitrate (Nos. l–9) were more degenerate than those with it as it is seen with the white spots on the surface of the former only. Nos. 8, 9, 17, and 18, which contained barium nitrate that damaged the potassium dichromate, belong to an exceptional case. Nos. 13, 14 and 15 have a very deep black surface, which may be the same with the black film of this section. However, only No. 13 which contained sodium nitrate in place of sodium sulfate was not vivid. Even the sodium nitrate can form a black film when the star is stored for such a long time. However the film is weaker than that from a sulfate. Other stars which contained guanidine nitrate, Nos. 10, 11, 12 and 16, are covered with a gray surface which shows it is still in the midst of forming the black film due to the low solubility of each sulfate.

3.3. The New Practical Method of Coating Magnesium Powder

Considering above experiments, the author presents the following coating method: 220 g of a hydrate of magnesium sulfate, $MgSO_4 \bullet 7H_2O$, 90 g of ammonium dichromate, $(NH_4)_2Cr_2O_7$, and 20 g of guanidine nitrate, $CN_3H_5 \bullet HNO_3$, are dissolved in 500 cc of water. 1000 g of magnesium powder is placed in a fairly large aluminum bowl and the solution is added to it. It is mixed, stirring by hand with gloves, until the powder colors uniformly brown. Then the powder is spread on a sheet of Kraft paper and dried well in the sun. When dried, it is passed through a 30 mesh sieve. The dust must not be inhaled because ammonium dichromate is poisonous.

With this method, the resistant black film is not formed in a short time even when the powder is soaked in a larger volume of the solution than the above. However, when the coating materials exist together with the magnesium powder, this method was far more effective at a corrosion test against ammonium perchlorate than the mechanical coatings using paraffin, linseed oil or polyester, which gave only a short time resistance of a few seconds or minutes.

4. Discussion and Conclusion

(1) The author presented the “minimum solubility law”, having an idea that the chemical reactions or degenerations inside of a consolidated firework mixture may be thought of as it is those among substances of a highly concentrated solution in water.

(2) The number of ions which can move in a consolidated mixture will be so small that the reactions proceed very slowly. Therefore, it has been very difficult to foresee the direction of reaction without experiences. However, with the help of this law we could overcome the difficulty.

(3) However, this method may not be applied to substances which do not dissolve into ions, metals or to acid or alkali forming substances, the solubilities of which in the acid or alkali are unknown.

(4) All the materials arranged in Table 1 are thought to have some relation in the firework field. The reactions with symbols are not all experimentally confirmed, but a few.

(5) Considering the results of two experiments, the foregoing of about eight year store and the latter supplemental, a method of new chemical coating of magnesium powder is presented: it is to use some sulfate which is easily soluble in water, except ammonium sulfate, some dichromate, and guanidine nitrate. The former two create a black film of CrO_2 and the latter makes the film stick well to the surface of magnesium grains adjusting the reaction rate.

(6) At the experiments with magnesium ribbon pieces, the coating was completed in one day soaking. However, with a magnesium powder, the reaction was very slow and takes more and more time. Therefore, it is better to cover the grains with a concentrated solution of the three materials in a proper ratio and to dry in the sun, as it is in ordinary case of coating. The temperatures must not be warm. The black film may be created during the store very slowly after the coating. It is still effective when the materials are not removed from the grains.

(7) The difference between the chemical coating and the ordinary physical coating may be: the former makes a resistant film in the course of the coating operation or later gradually makes it slowly in the course of the store, and the latter makes it only in the course of the operation. Experiments showed the former was far more effective than the latter by ordinary physical methods.

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Burning Rate and Grain Size of Component Materials of Pyrotechnic Mixtures

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ABSTRACT

It has been generally believed that the finer the grain size, the faster the burning when we select the component materials of a pyrotechnic mixture. It is not always true because a small explosion occurred in the past when we tested a smoke mixture, although it contained a dye of very coarse grains.

The purpose of this paper is to make clear the general mechanism of the burning rate of pyrotechnic mixtures on the standpoint of the grain size of component materials of pyrotechnic mixtures.

Experiments on burning rate were carried out with four types of mixtures changing the grain size of the component materials:

(a) base mixtures of oxidizer (conventional materials as potassium chlorate, potassium perchlorate or ammonium perchlorate) and fuel (accroides resin),

(b) mixtures of the base and an inert material (clay),

(c) mixtures of the base and a semi-inert material (barium nitrate),

(d) mixtures of an explosive of synthesized simple substance (potassium picrate) and an inert material (clay).

All the materials except potassium picrate were sieved to obtain grains of six class sizes.

With decreasing the grain size of the component materials, some mixtures increased and some decreased the burning rate. In other cases there were grain sizes which gave the smallest burning rate: the burning rate at first decreased and then increased. In general, the burning reaction seemed to be stabilized as the grain size decreased. These effects will help the designing of pyrotechnic mixtures for various purposes.

I. Introduction

The objective of this work was to find possibly the general law of the relation between the burning rate and grain size of component materials of pyrotechnic mixtures.

As a representative case, four types of mixture were experimentally examined:

(a) base mixtures of oxidizer and fuel,

(b) mixtures of the base and an inert material,

(c) mixtures of the base and a semi-inert material,

(d) mixtures of an explosive of simple synthesized substance and an inert material.

II. Experimental

2.1. Materials and classification of their grain size

As the oxidizers three conventional substances, potassium chlorate from Nippon Soda Co., potassium perchlorate from Nippon Carlit Co. and ammonium perchlorate from Kanto Kagaku Co. were used. As the fuel accroides resin[1] was used due to its wide use in firework field**.** It was obtained through Daiichi Yakuhin Kogyo Co. As the inert material a kind of clay of Kanto loam was used. As the semi-inert material barium nitrate, which is not easily decomposed at ordinary flame temperatures (1500–2200 °C), from Barite Industry Co. was used. As the explosive potassium picrate was synthesized with picric acid (a reagent) and potassium carbonate by the author.[2]

For the classification of grain sizes of the materials six types of sieve were used:

14 mesh with openings of 1.40 mm, used in our work room,
20 mesh with openings of 0.77 mm, used in our work room,
32 mesh with openings of 0.495 mm, standard,
48 mesh with openings of 0.295 mm, standard,
65 mesh with openings of 0.208 mm, standard,
150 mesh with openings of 0.104 mm, standard.

2.2. Preparation of samples

The oxidizers or the semi-oxidizer in powdered state were once dissolved in hot water and recrystallized by cooling slowly to obtain possibly large crystals. The crystals were roughly ground in a porcelain mortar and sieved using the sieves above mentioned. The grains of each material were classified as it is seen in Figure 1.

For example, G3 means the grains that passed the 32 mesh sieve and did not pass the 48 mesh sieve.

The fuel, accroides resin, in powdered state was once melted in a 120 °C oven to a black mass. Then it was ground and sieved as it was with the oxidizers.

The inert material, clay, was prepared by crushing well dried clods of the clay by a hammer and ground in the mortar to proper grain sizes, which were classified by the same way as before.

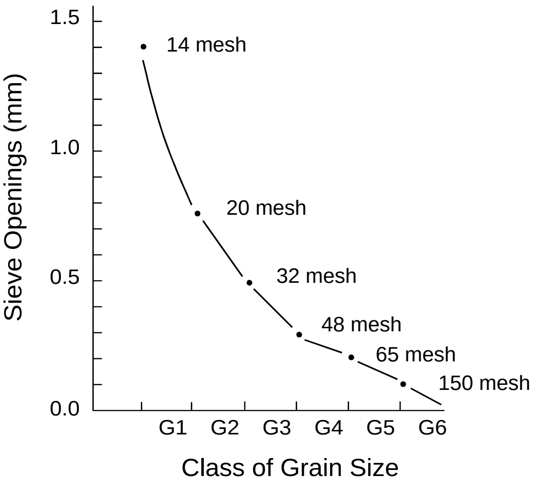

Figure 1. Classification of grain sizes.

Base mixtures to see the effect of the grain sizes were prepared with 36 types as shown in the matrix 1 (below) for each oxidizer. Each element is denoted by three letters: the first G means the “grain”, the second letter means the grain class of the accroides resin and the third, that of the oxidizer. For example, G23 means a mixture of the accroides resin of the second class grain size and the oxidizer of the third class. The weight ratio of the oxidizer and accroides resin was 80/20, the value of which was common to all element mixtures.

Fifteen grams of each element mixture without binding material was put into a Kraft tube of 27 mm inside diameter, 50 mm long and having a wall thickness of 1 mm in a split mold with three segments. It was pressed under a pressure of 2.8 ton/cm^2 for five seconds using a press. For ignition a small quantity of a fine magnesium powder was placed on the one end surface adding a small piece of black match (Figure 2).

Matrix 1:

G11	G12	G13	G14	G15	G16
G21	G22	G23	G24	G25	G26
G31	G32	G33	G34	G35	G36
G41	G42	G43	G44	G45	G46
G51	G52	G53	G54	G55	G56
G61	G62	G63	G64	G65	G66

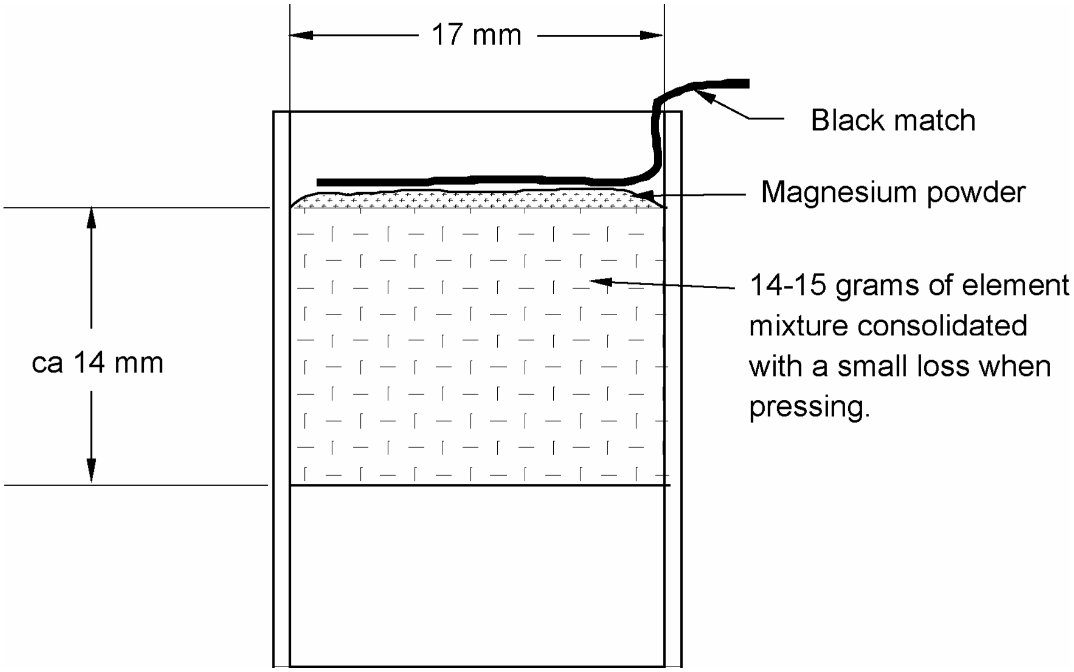

Figure 2. Sample for burning test.

Mixtures of the base and the inert material, clay, were prepared with 18 types as shown in the Matrix 2 for each oxidizer. As the base the element mixture G66 was used (Matrix 2). Each element is denoted by 7 letters: the first G66 means the element mixture in the former matrix of the base in the foregoing page (matrix 1), the next two letters, 1C to 6C, mean the class of grain size of the clay and the next figures, 10 to 30, mean the weight percentage in each element mixture. For example, G66-4C20 means a mixture of 20% clay of 4th class of grain size and 80% G66 element mixture. The G66 is a mixture of the smallest grain size of both the oxidizer and fuel. Mixtures of the base and the semi-inert material, barium nitrate, were prepared in the same way as the Matrix 2 (Matrix 3). In the Matrix 3 the symbol B means barium nitrate in place of C in the Matrix 2. Other symbols are the same as those of the Matrix 2.

Matrix 2:		
G66-1C10	G66-1C20	G66-1C30
G66-2C10	G66-2C20	G66-2C30
G66-3C10	G66-3C20	G66-3C30
G66-4C10	G66-4C20	G66-4C30
G66-5C10	G66-5C20	G66-5C30
G66-6C10	G66-6C20	G66-6C30

Matrix 3:		
G66-1B10	G66-1B20	G66-1B30
G66-2B10	G66-2B20	G66-2B30
G66-3B10	G66-3B20	G66-3B30
G66-4B10	G66-4B20	G66-4B30
G66-5B10	G66-5B20	G66-5B30
G66-6B10	G66-6B20	G66-6B30

The element mixtures without binding material were consolidated by the same method as those of the Matrix 1 as the samples to use for the burning test.

The explosive of simple substance, potassium picrate, was mixed with the clay of six size classes of grains. The weight ratio of the picrate to the clay was 90/10. Two grams of each element mixture were pressed into a stainless steel tube of 11 mm inside diameter, 60 mm long and having a wall thickness of 1 mm.

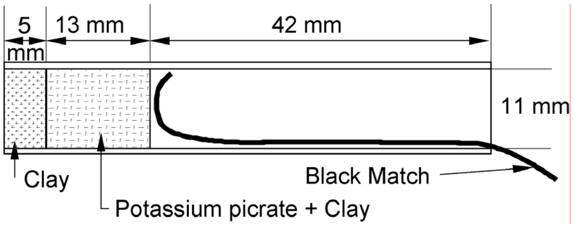

Figure 3. Sample of burning test of potassium picrate mixture.

Matrix 4:

PP-1C	PP-2C	PP-3C	PP-4C	PP-5C	PP-6C

2.3. Burning test and the result

The number of the sample for each matrix element was one. The samples were placed in the open air and the burning times were measured by stop watch. The results are shown with following matrixes (1)–(10) and Figures 4–13.

2.3.1. Burning rate in mm/s with the mixtures of oxidizer and accroides resin following the Matrix 1

(1) Potassium chlorate and accroides resin

0.77	0.74	0.78	1.09	0.80	1.04
0.79	1.07	0.93	0.84	0.99	1.17
1.16	1.10	1.08	1.09	1.12	1.06
1.05	1.16	1.22	1.45	1.42	1.71
1.23	1.24	1.37	1.61	1.61	1.97
1.18	1.19	1.59	1.68	1.43	1.67

(2) Potassium perchlorate and accroides resin

0.17	0.59	0.71	0.66	0.82	0.76
0.85	0.75	0.80	0.87	0.65	0.93
0.79	0.85	0.87	0.86	0.92	1.18
0.84	0.85	0.95	1.07	1.28	1.09
0.79	0.90	1.00	1.15	1.29	1.33
0.87	0.99	—	1.04	1.11	1.19

(3) Ammonium perchlorate and accroides resin

0.54	0.50	0.46	0.50	0.56	0.52
0.56	0.61	0.60	0.61	0.60	0.67
0.50	0.62	0.65	0.76	0.73	0.87
0.63	0.60	0.77	0.84	0.88	0.94
0.63	0.68	0.80	0.94	1.02	1.14
0.69	0.81	0.88	1.03	1.15	—

2.3.2. *Burning rate in mm/s with the mixtures of the base G66 and the inert material, clay. The data obtained are arranged following the Matrix 2.*

(4) $KClO_3$ base		
1.10	1.29	0.87
1.01	0.93	0.66
1.00	1.02	0.81
1.08	0.98	0.97
1.31	1.23	1.12
1.38	1.61	1.97

(5) $KClO_4$ base		
1.07	0.82	0.88
0.96	0.85	0.65
1.04	0.88	0.87
1.00	0.74	0.57
1.14	0.72	0.57
1.06	1.27	0.99

(6) NH_4ClO_4 base		
1.25	1.02	0.92
1.22	1.01	0.87
1.06	1.01	0.87
1.11	1.09	0.81
1.55?	0.99	0.93
1.28	1.14	1.14

2.3.3. *Burning rate in mm/s with the mixtures of the base G66 and the semi-inert material, barium nitrate. The data are arranged following the Matrix 3.*

(7) $KClO_3$ base		
1.24	0.98	0.79
1.09	1.03	0.78
1.17	0.98	0.78
1.17	0.92	0.85
1.17	1.04	0.89
1.18	1.08	1.10

(8) $KClO_4$ base		
1.01	0.86	0.65
1.00	0.88	0.72
0.94	0.92	0.75
0.96	0.89	0.79
0.94	0.93	0.86
1.06	1.12	0.88

(9) NH_4ClO_4 base		
1.19	0.94	1.03
1.24	1.03	0.93
1.19	1.06	1.02
1.11	1.01	0.87
1.14	0.84	0.72
1.09	0.85	0.58

With the element mixtures, G66-6B20, G66-4B30, G66-5B30 and G66-6B30 of NH_4ClO_4 base a flame of very deep green was produced.

2.3.4. *Burning rate in mm/s with the explosive of simple substance, potassium picrate, mixed with 10% inert material, clay. The data are arranged following the Matrix 4.*

(10)	5.42	4.28	4.19	3.94	3.16	4.33

A whistling noise was produced from each element mixture. It seemed the tone of the whistle increased as the grain size of the clay decreased.

2.3.5. *Graphical expression of the results*

All of the results which are expressed by matrixes from (1) to (10) are further graphically expressed by the following figures.

With Figures 4, 5 and 6, which concern the mixtures of oxidizer and fuel, the left curves are mainly to see the effect of the grain sizes of fuel, accroides resin, and the right of the effect of oxidizer. With Figures 7–12, which concern the mixtures of the base G66 and the inert material, clay, or semi-inert material, barium nitrate; the left curves are mainly to see the effect of the grain sizes of the inert or semi-inert material, and the right the effect of the mixing ratios of the material to the base mixture G66. Figure 13 shows the effect of the grain sizes of the inert material, clay, when ten percentages of clay were mixed to potassium picrate. (1)–(10) show the corresponding matrix number.

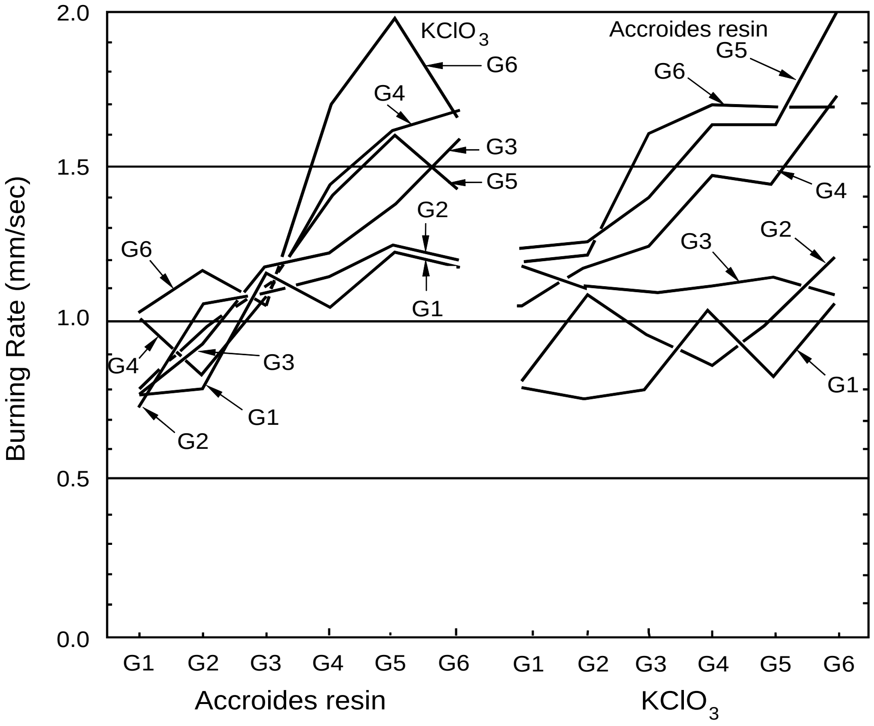

Figure 4. Potassium chlorate and accroides resin, (1).

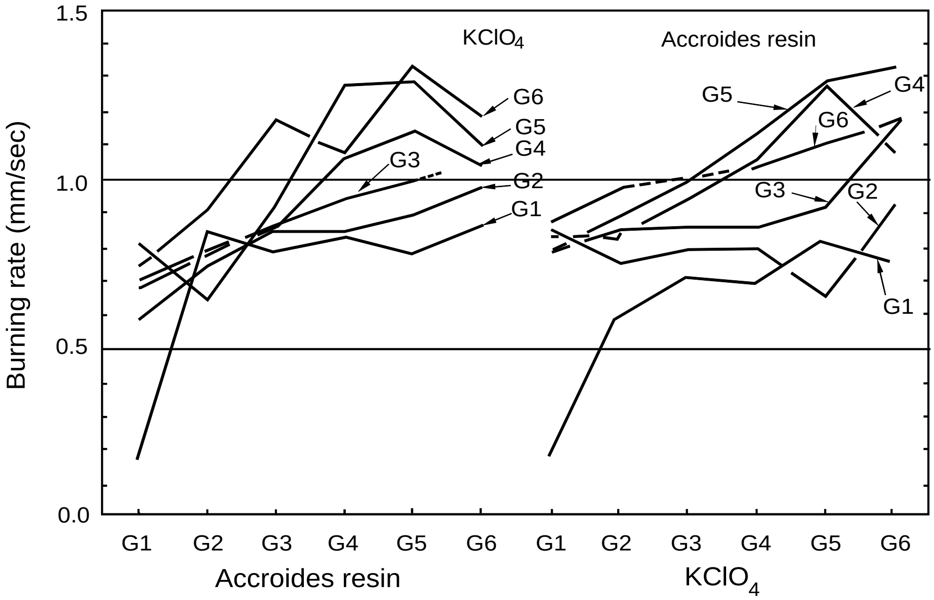

Figure 5. Potassium perchlorate and accroides resin, (2).

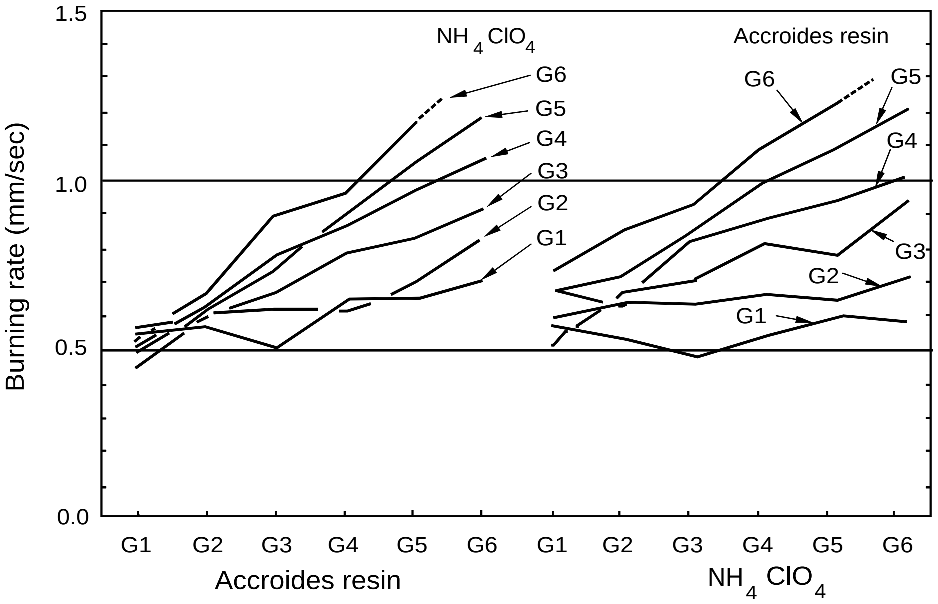

Figure 6. Ammonium perchlorate and accroides resin, (3).

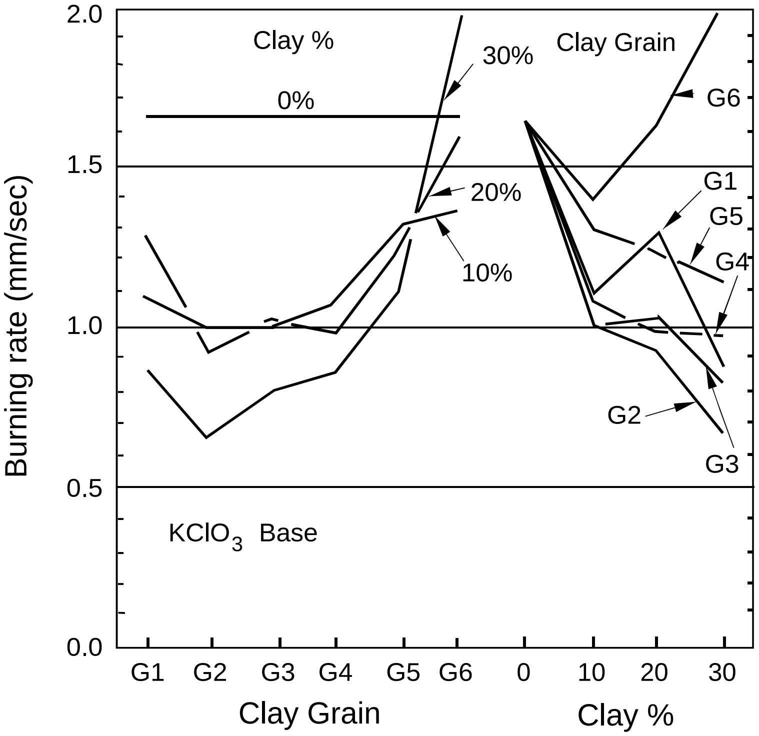

Figure 7. Potassium chlorate base G66 and clay, (4).

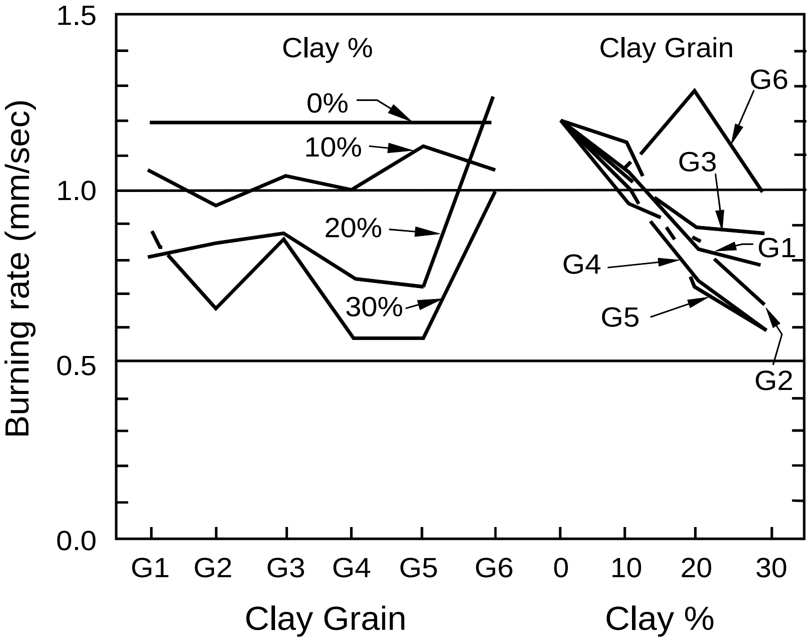

Figure 8. Potassium perchlorate base G66 and clay, (5).

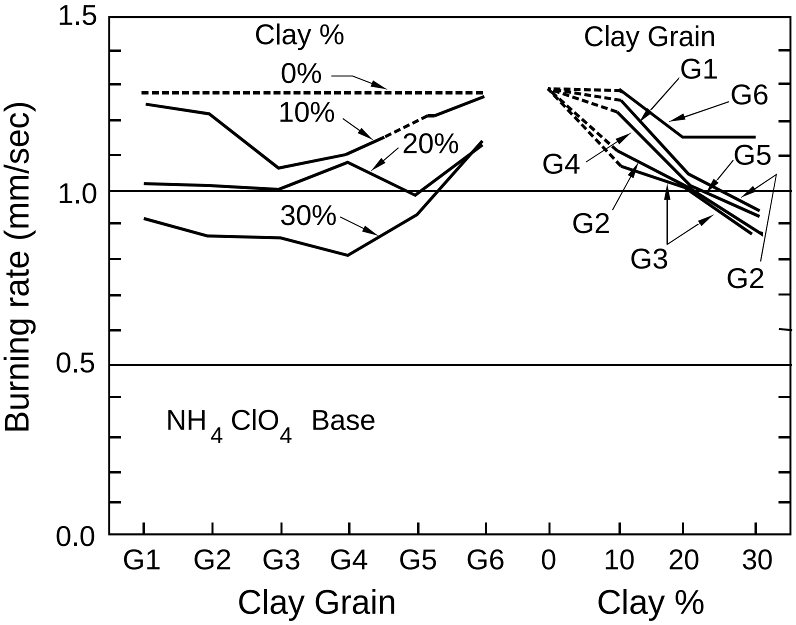

Figure 9. Ammonium perchlorate base G66 and Clay, (6).

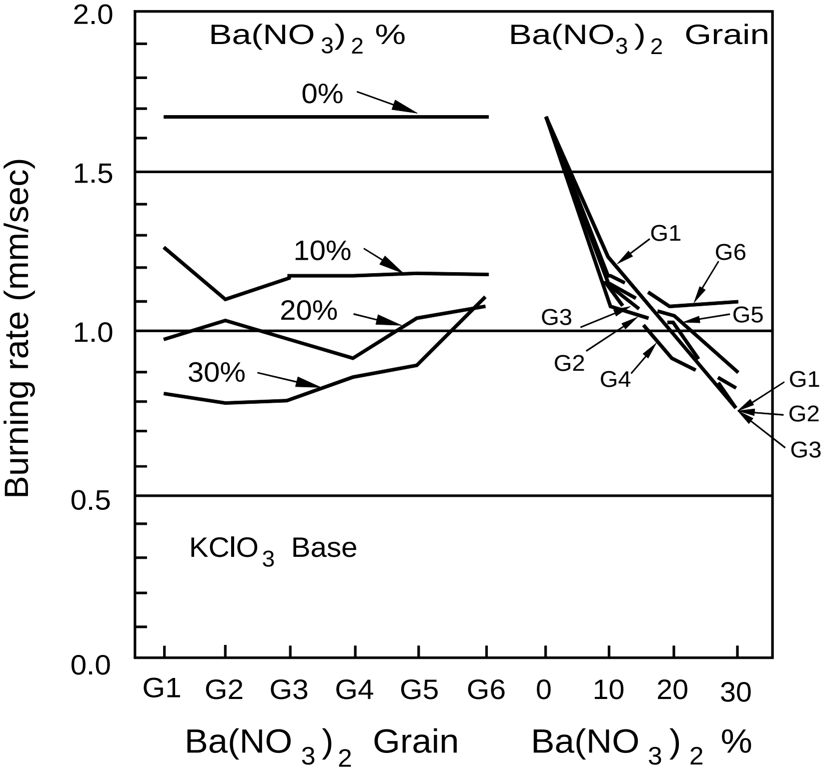

Figure 10. Potassium chlorate base G66 and barium nitrate, (7).

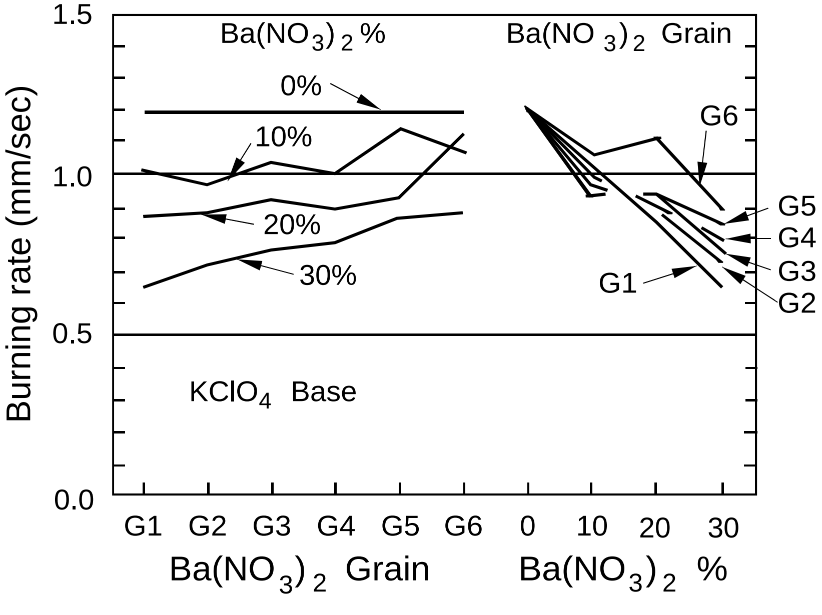

Figure 11. Potassium perchlorate base G66 and barium nitrate, (8).

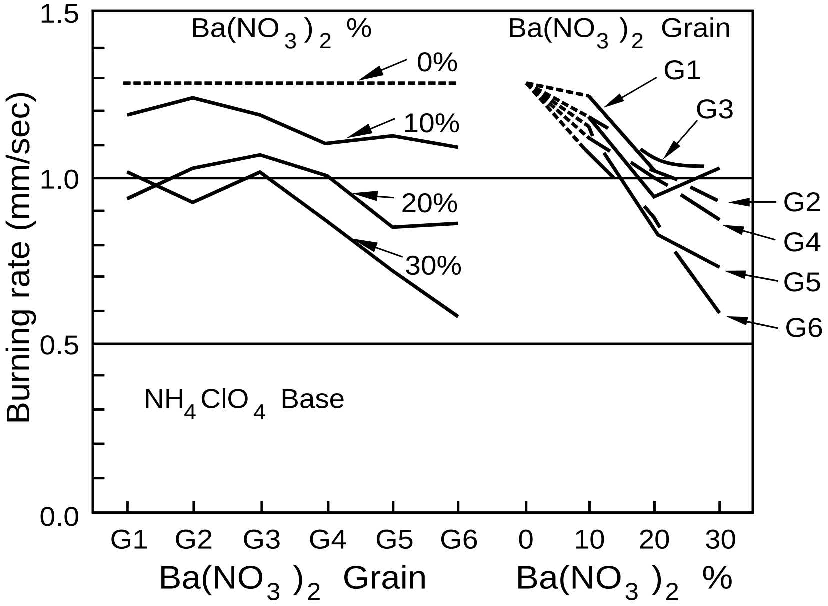

Figure 12. Ammonium perchlorate base G66 and barium nitrate, (9).

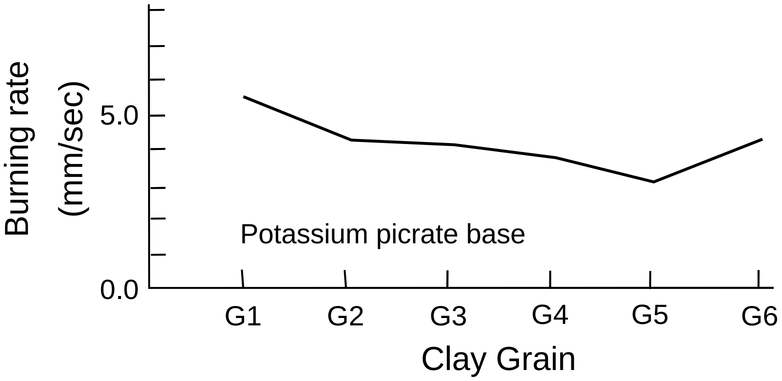

Figure 13. Potassium picrate base and clay, (10).

III. Discussion and Conclusion

(1) The Mixtures of Oxidizer and Fuel, Accroides Resin

This is the most general and fundamental case of burning. With ammonium perchlorate base the mixtures most smoothly burned with steadily increasing the burning rate as the grain size of the oxidizer or fuel decreased (Figure 6 or Matrix (3)). The large grain sizes, G1 or G2, of the fuel had almost no effect on the burning rate. The burning rate with G6 of the fuel was twice as large as that with G1. With the grain sizes of ammonium perchlorate the same effects as those of the fuel were observed.

In the case of potassium chlorate or perchlorate base of the effects were somewhat different from those of the above case. (Figures 4, 5 or Matrices (1), (2)). The fuel grain sizes G1 or G2 gave unstable burning effects as it is seen with the zigzag curves in the right side of Figure 4 or 5 nearly irrespective of grain size of the oxidizer. It should be remembered the mixture which gave the largest burning rate was not G66, but G56.

(2) The Mixtures of the Base Mixture G66 and Inert Material, Clay

The G66 mixture, a mixture of smallest grains of the oxidizer and fuel, was selected due to its highest burning stability to see the effect of the inert material. The clay was selected as the inert material due to its low reactivity when burning with a mixture of no magnesium.

The burning rate generally decreased as the percentage of the inert material increased. There were grain sizes of the inert material, clay, which gave minimum burning rate for each mixture: G2 for the potassium chlorate base, G4 or G5 for the potassium perchlorate base and G4 for the ammonium perchlorate base. Such a tendency very clearly appeared with the chlorate base. (Figures 7–9 or Matrixes (4)–(6))

It should be remembered the burning rate increased as the percentage of the clay increased when the minimum grain size G6 was used, especially with the chlorate base. The burning rate of the mixture, G66-6C30, exceeded that of G66 which contained no clay. Such a positive effect certainly came from the fact that even an inert material takes part in some chemical reaction at high temperatures when its grains are very fine.

(3) The Mixtures of the Base Mixture G66 and Semi-Inert Material, Barium Nitrate

Barium nitrate has an oxidizing power, but is not easily dissociated by heating.

The burning rate of the mixtures of this type decreased as the percentages of the barium nitrate increased. On the other hand, the burning rate increased as the grain size of the barium nitrate decreased with the potassium chlorate or perchlorate base. However, with the ammonium perchlorate base it went reversely, i.e., the rate decreased with decreasing the grain size of the barium nitrate. This was a notable effect of the ammonium perchlorate base. When the grain size of the barium nitrate was 5G or 6G with 20–30% content, a very deep green flame was produced. It might be due to some different burning reaction from others which was caused by the small size grains.

(4) The Mixtures of a Simple Explosive, Potassium Picrate, and an Inert Material, Clay

Ten percentages of the clay decreased the burning rate as the grain size of the clay decreased. However, the rate increased at last with the grain size G6. The smallest grains of the clay gave the highest tone of the whistling sound.

References

1) R. Lancaster, *Fireworks, Principles and Practice*, 2nd ed., 1992, p 43.

2) *ibid*., p 277.