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An Example of Negative Explosives: Magnesium Sulfate/Magnesium Mixture

Takeo Shimizu
Koa Fireworks Co., 350–12 Hidaka-machi, Saitama-ken, Japan

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

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:

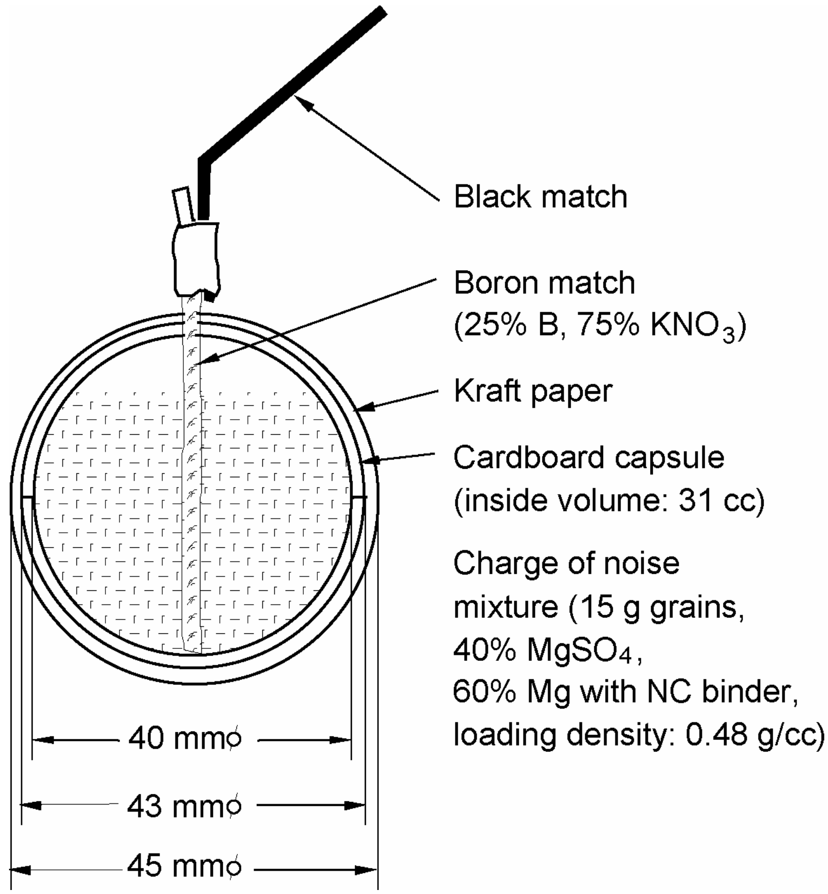


Figure 1. A test sample of capsule type.

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

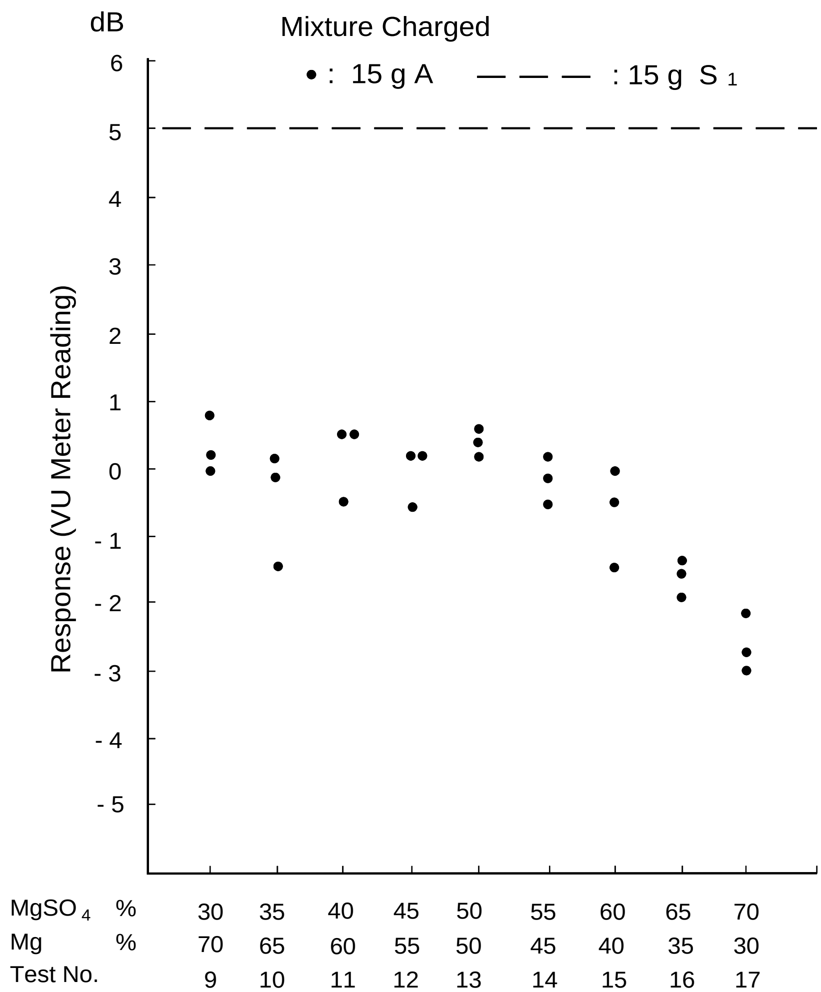


Figure 2. The noise intensities by the response of recorder relative to the weight ratio $MgSO_4$/Mg.

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

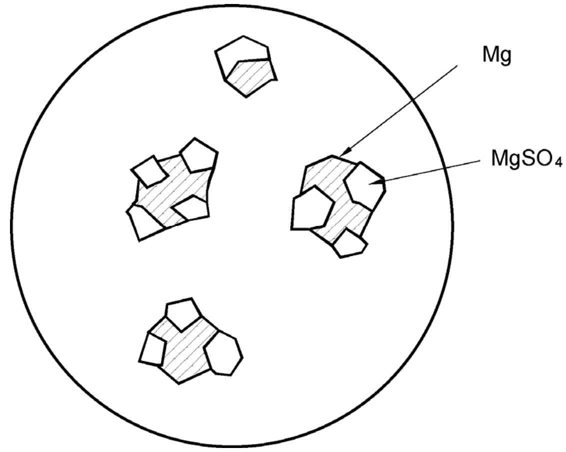


Figure 3. A sketch of small grains of mixture A or B through microscope.

were examined in comparison with that from the standard mixture S2. The results are plotted in Figure 4.

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.

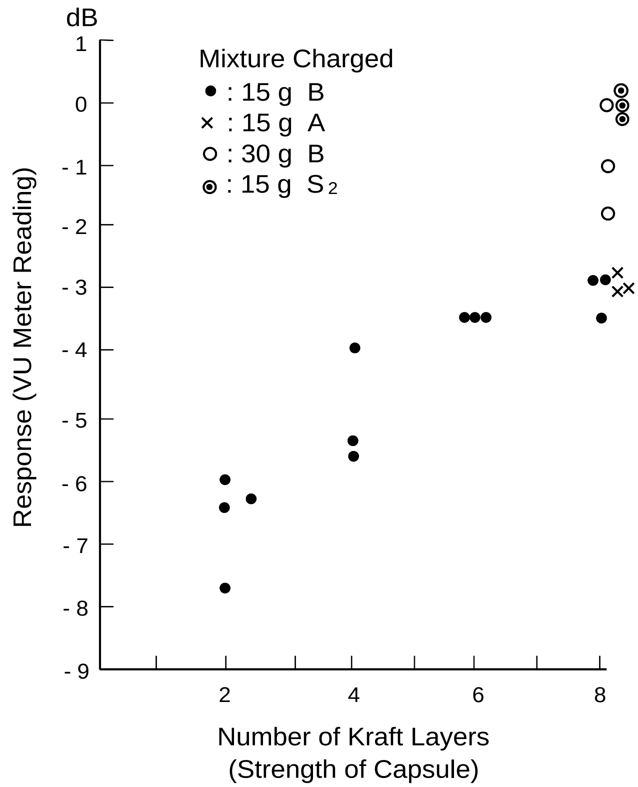
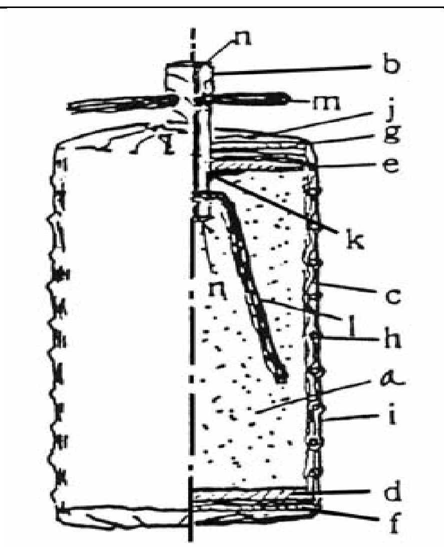


Figure 4. Noise intensities relative to the strength of capsule, quantity of charge and types of mixture A, B and S2.

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.

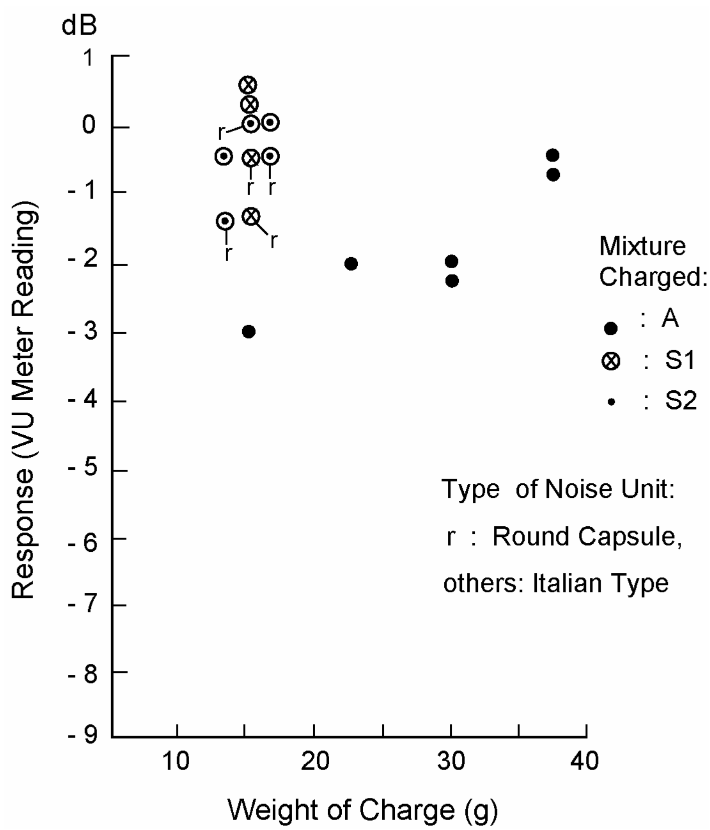


Figure 6. Noise intensities relative to the quantity of charge with Italian shell type noise unit.

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 ($MgSO_4 \cdot 7H_2O$/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

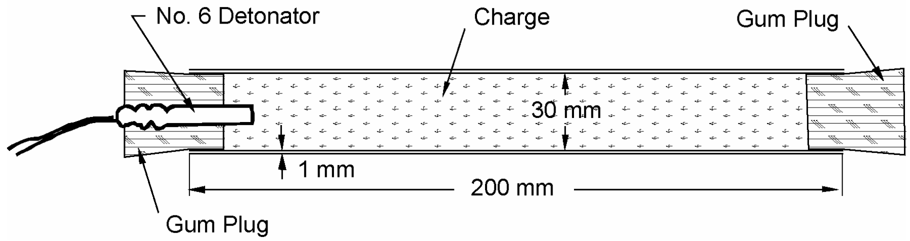


Figure 7. Sample for iron tube test.

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.

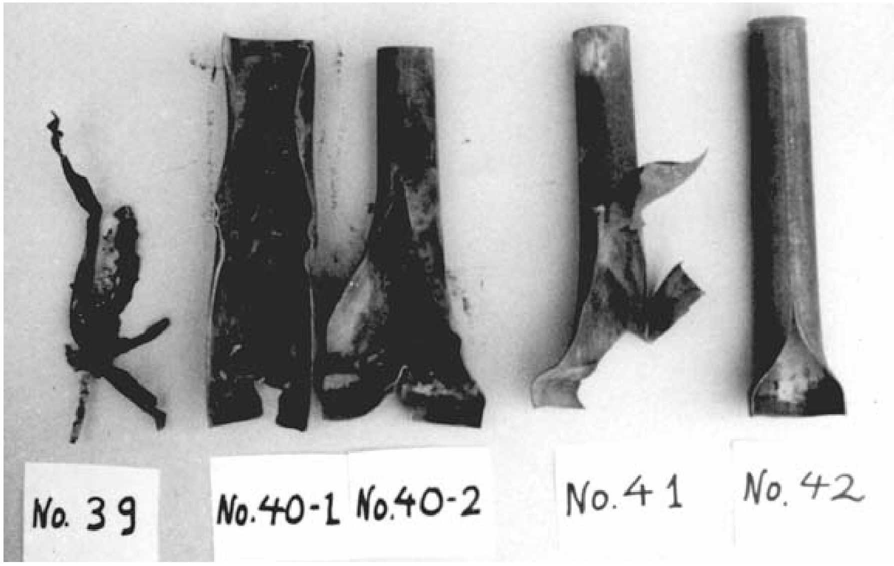


Figure 8. The debris obtained after the iron tube test.

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
1	●	×	×	×	11	∇	∇	×	×
2	×	×	×	×	12	∇	∇	×	∇
3	●	⊗	×	×	13	∇	∇	◎	×
4	●	×	×	×	14	∇	∇	◎	∇
5	●	×	×	×	15	∇	∇	◎	×
6	●	●	×	×	16	∇	∇	◎	×
7	●	×	×	×	17	∇	∇	×	×
8	●	×	×	×	18	∇	∇	◎	×
9	●	●	×	×	19	∇	∇	◎	×
10	●	●	×	×	20	∇	∇	◎	×

Symbols:	
×	: no ignition
∇	: smoothly propagated
◎	: actively propagated
⊗	: a small fire appeared, but not propagated
●	: detonated

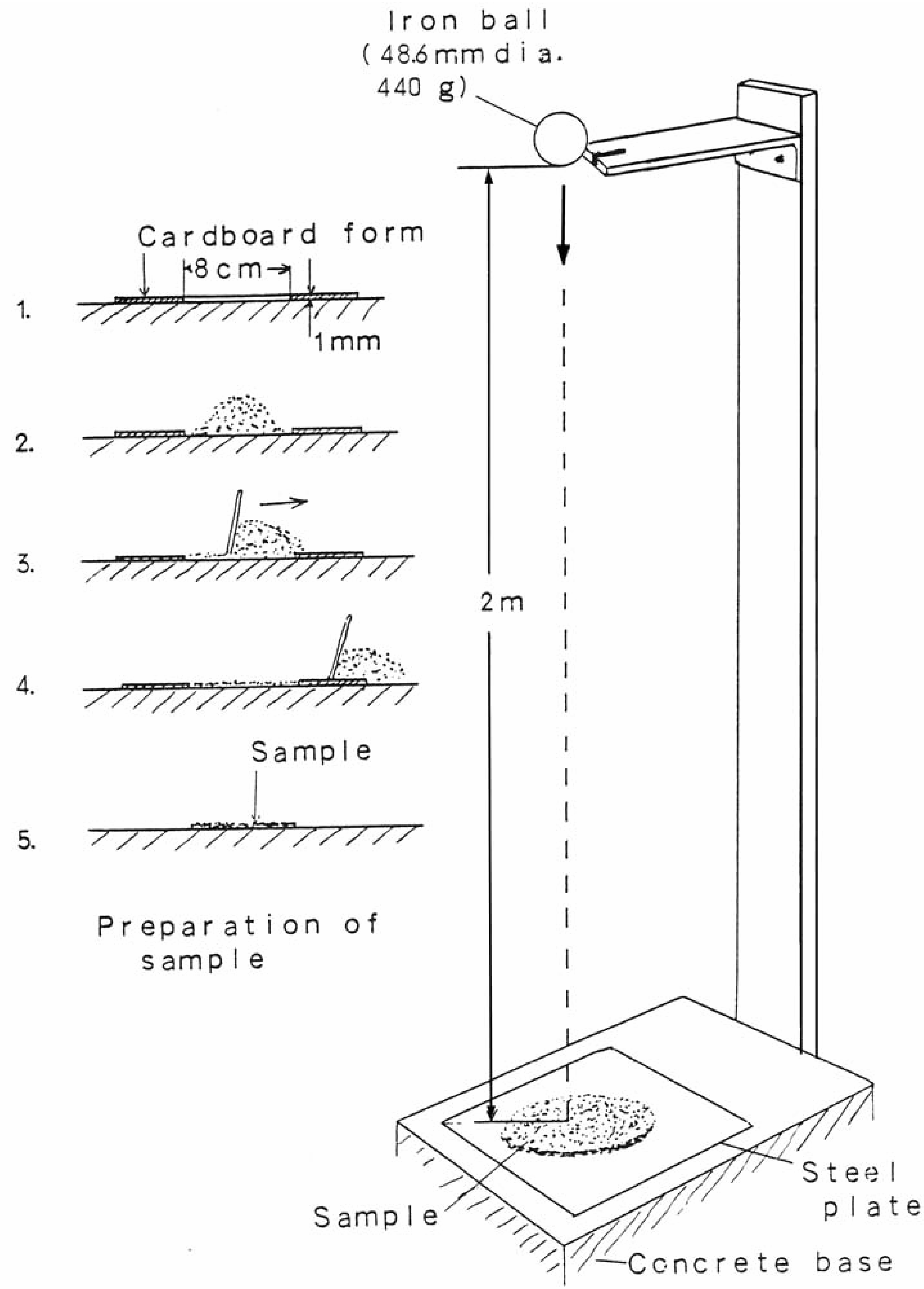


Figure 9. Fire propagation test apparatus.

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.

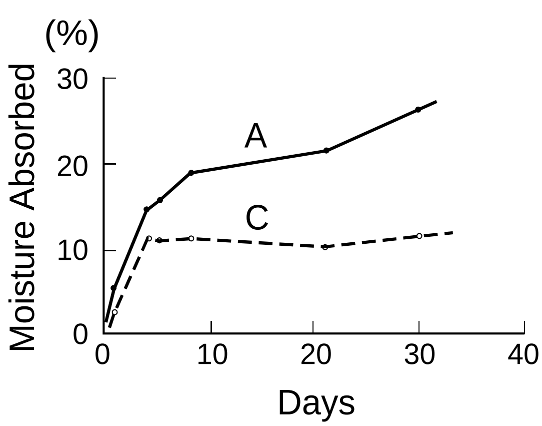


Figure 10. The result of moisture absorption test.

The value of noise absorption increased with time, especially with mixture A. In the literature cited below[2] it said that $MgSO_4 \cdot 7H_2O$ 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 ($MgSO_4 \cdot 7H_2O$/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% $MgSO_4 \cdot 7H_2O$/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:

$$\frac{\text{Force of mixture C}}{\text{Force of B. P.}} = \frac{\text{Flight distance by mixture C}}{\text{Flight distance by B. P.}} \times \frac{\text{Charged weight of B. P}}{\text{Charged weight of mixture C}} = \frac{43.6}{73.4} \times \frac{1}{5} = \frac{1}{8} \left(\text{B. P.: black powder}\right)$$

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.

References

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