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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.

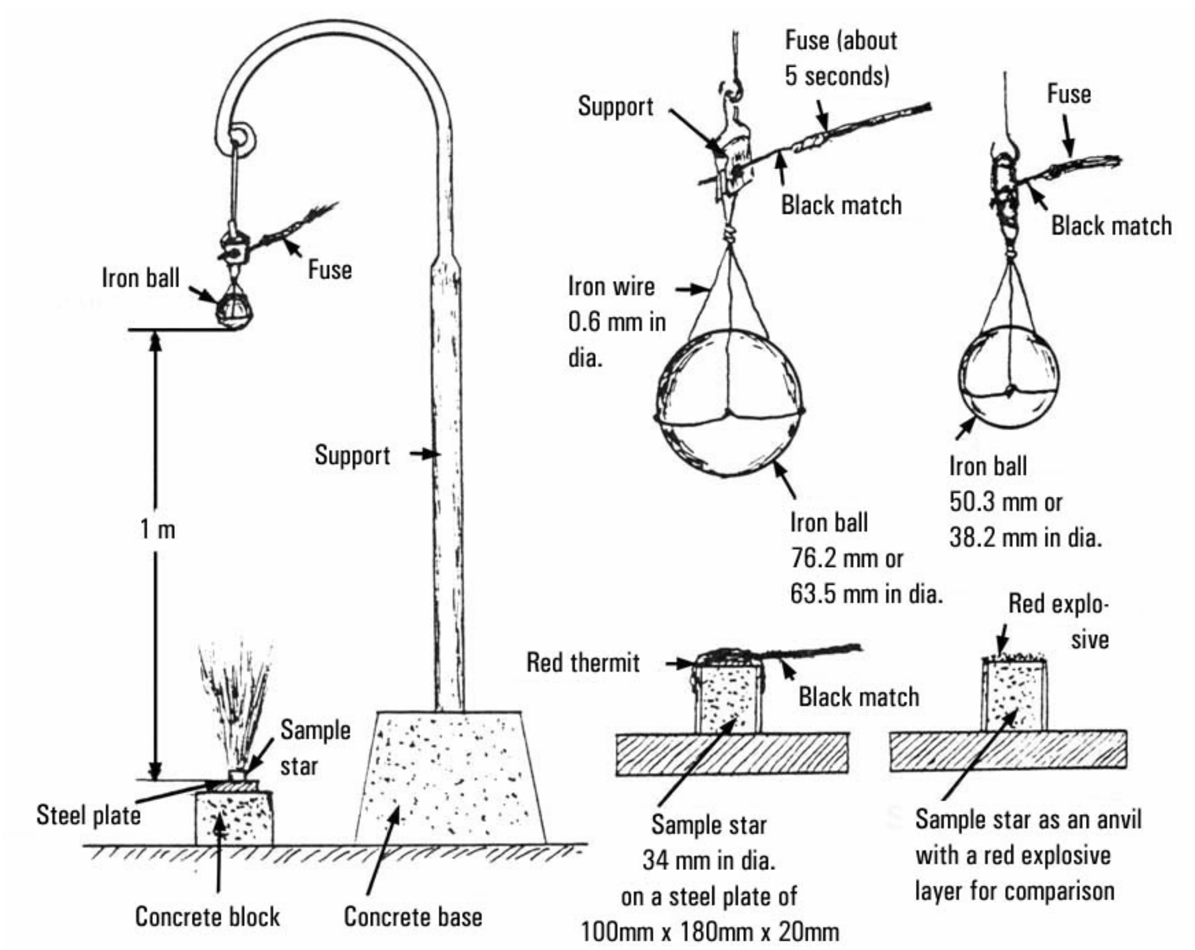

Figure 1. Apparatus for testing sensitivity of burning surface layer by dropping an iron ball onto a burning sample star.

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				Effect of dropping iron ball: 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

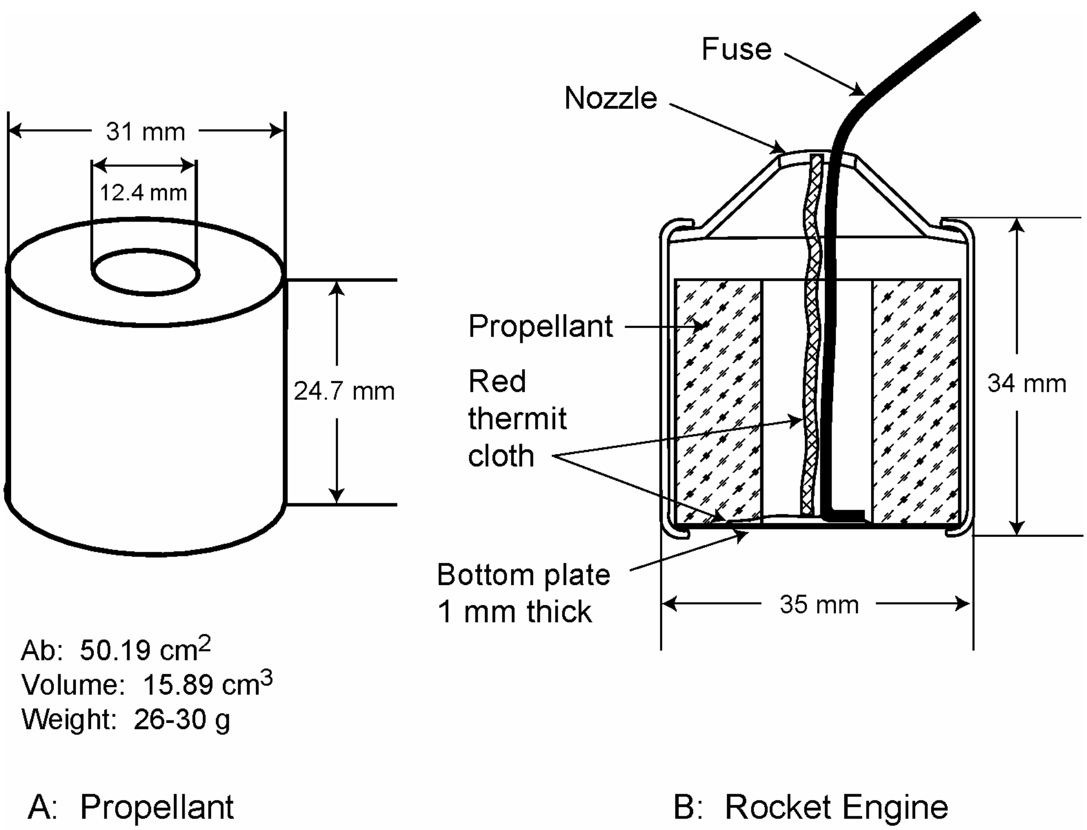

Figure 2. Sample rocket propellant and engine.

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_4ClO_4 + Polyester	1.0 s □	5.0 s	1.0 s	3.0 s	0.8 s	0.8 s	– □
F NH_4ClO_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.

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