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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	$CaC_2O_4•H_2O$	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	$CaSO_4•1/2H_2O$	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	$Al_2(SO_4)_3•18H_2O$	1.214	—	x	x	x
21	$FeSO_4•7H_2O$	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	$Mg_3(Si_4O_{10})•(OH)_2$	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.

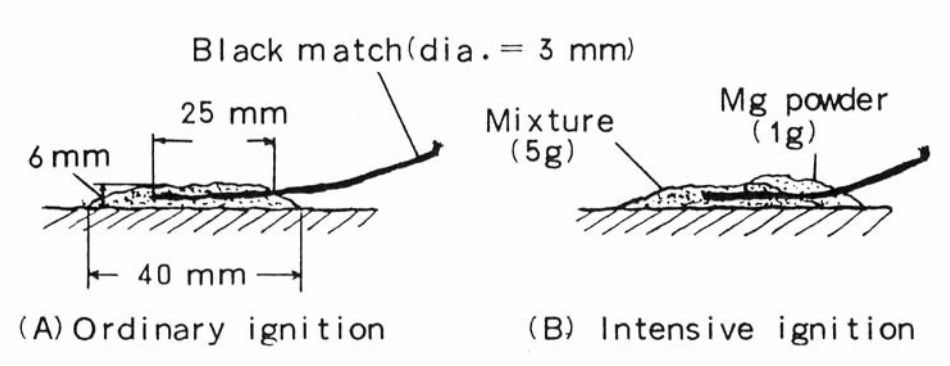

Figure 1. Burning test on the ground.

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).

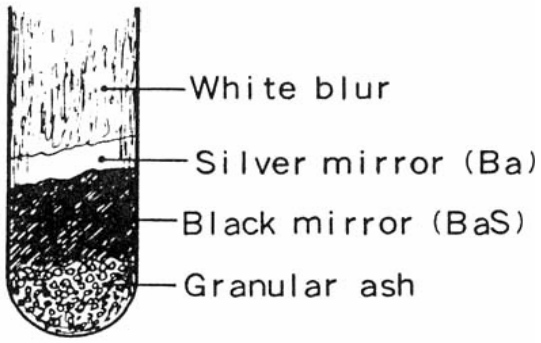

Figure 2. An example of the outside view of test tube after the heating test ($BaSO_4$).

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.

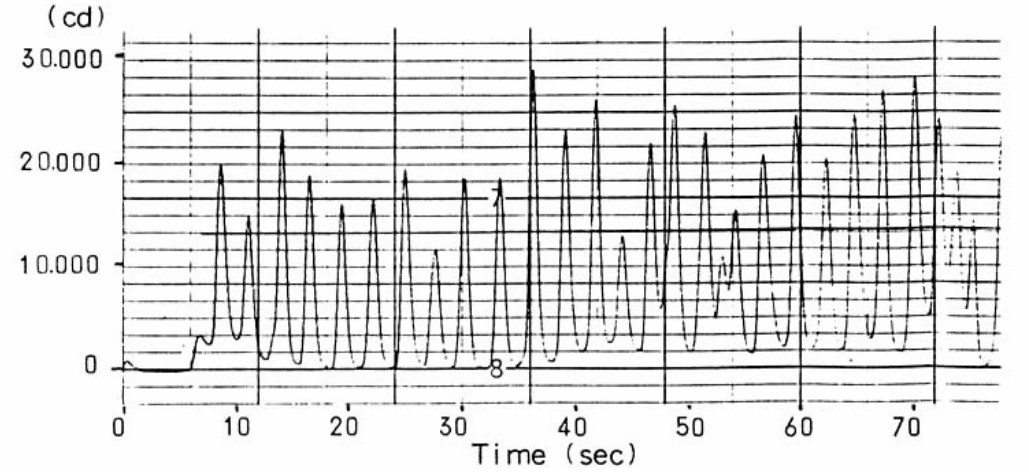

Figure 3. From the burning test of a flare of $Na_2C_2O_4$.

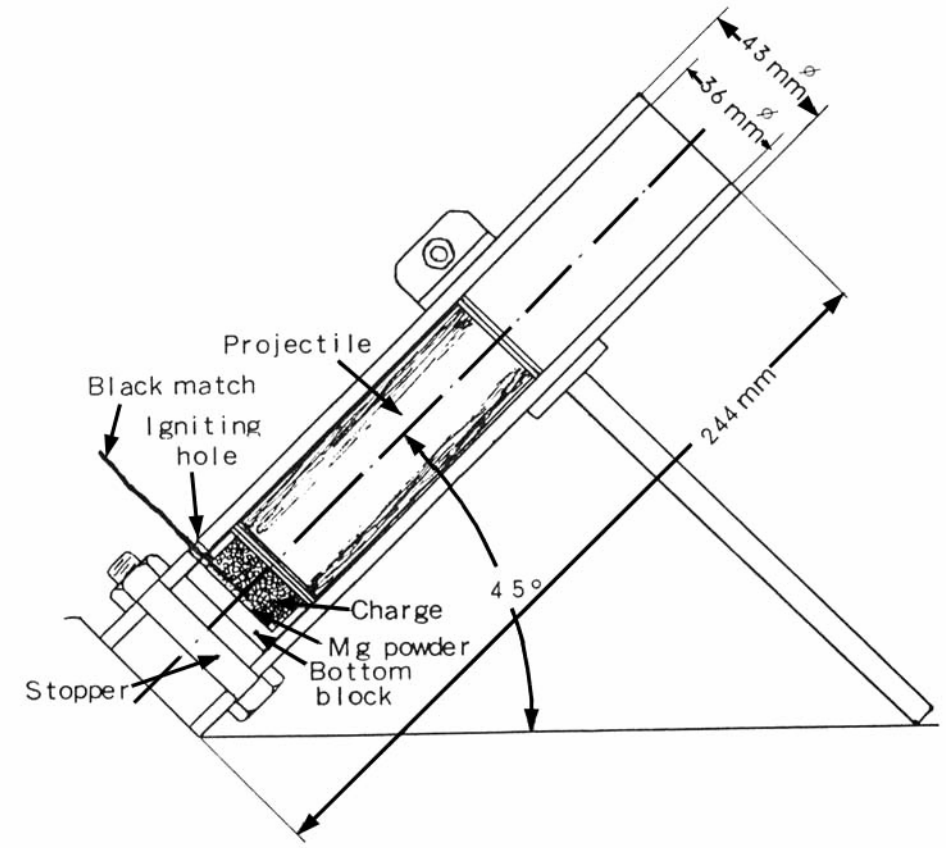

Figure 4. The iron mortar for firing test.

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, $FeSO_4 \cdot 7H_2O$; 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	by impact	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.

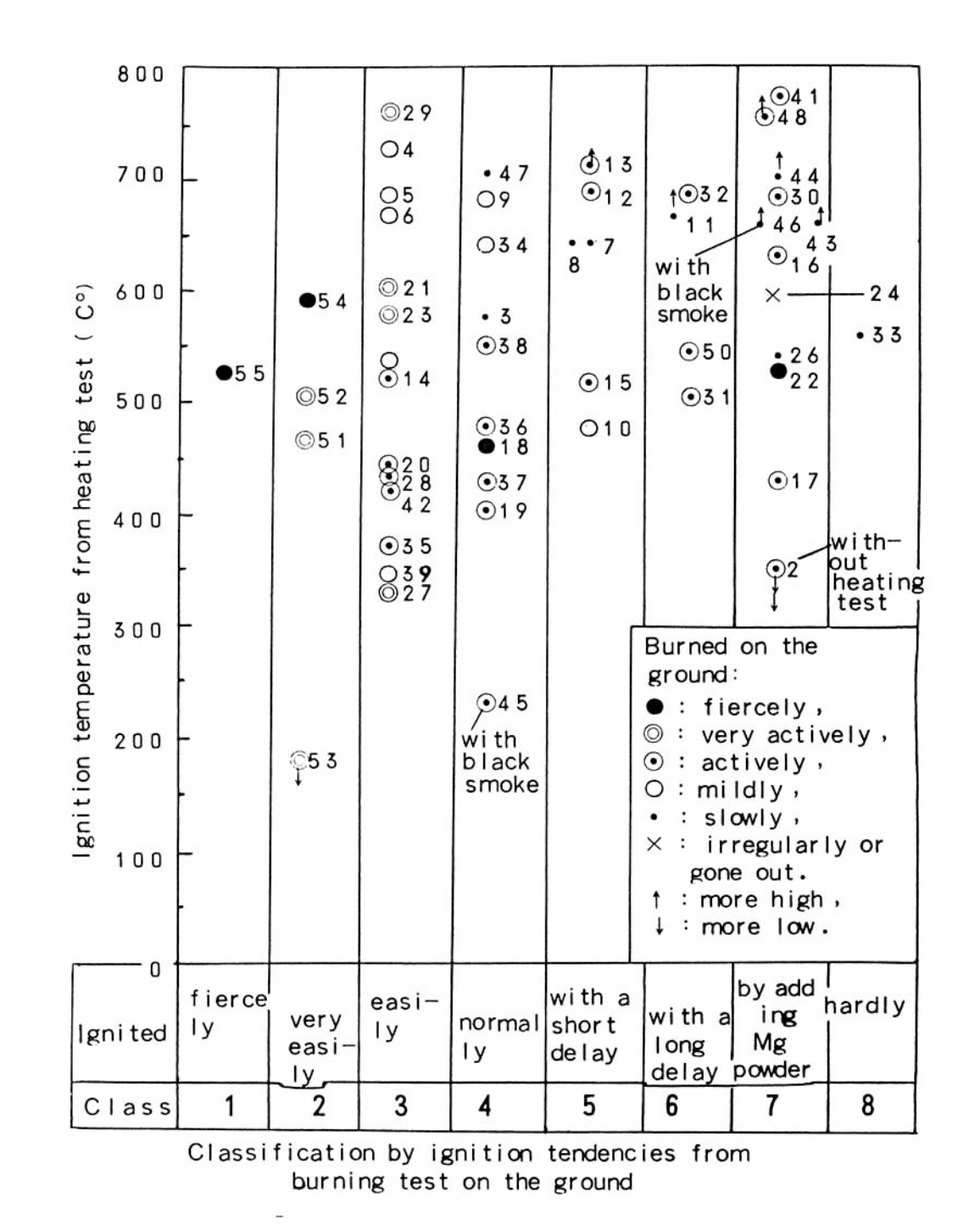

Figure 5. Ignition tendencies, ignition temperatures and burning conditions of mixtures.

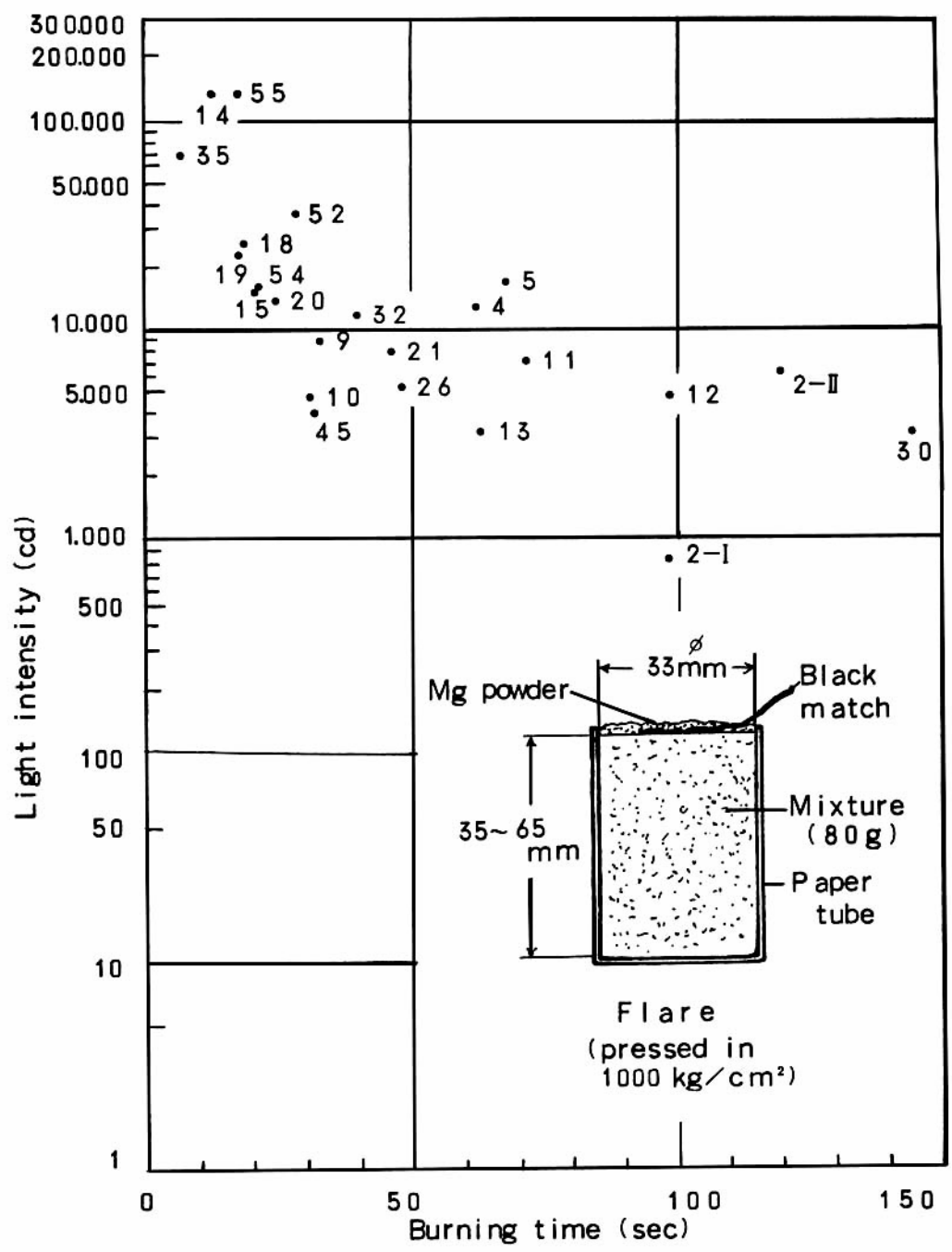

Figure 6. The results of the burning test of flares.

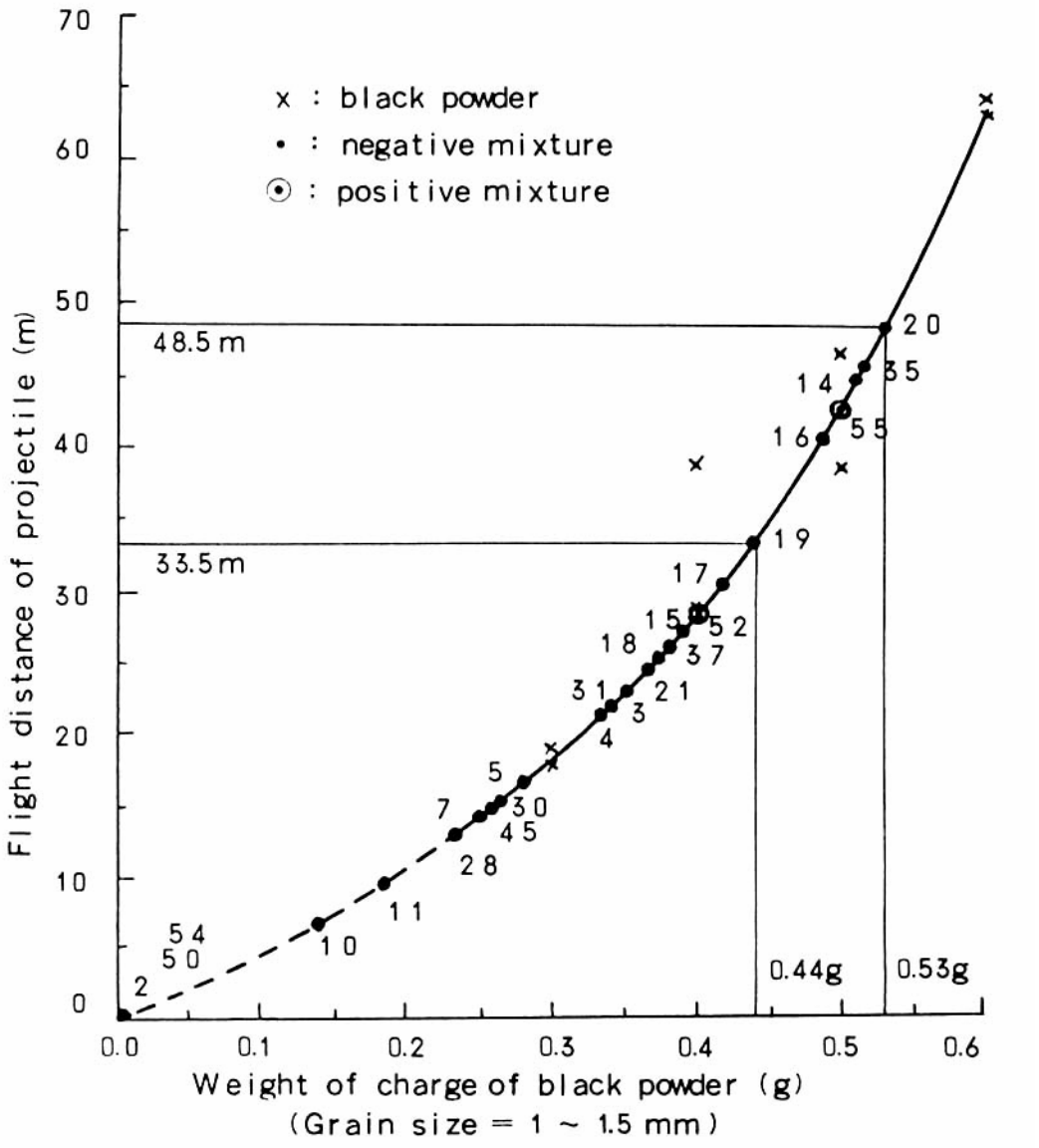

Figure 7. The results of the firing test comparing with those of Black Powder charges.

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 fire-work 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 ($A1_2$ $(SO_4)_3$•$18H_2O$) 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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