

## Development of heat resistant industrial explosives

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When explosives are heated under acidic environment due to metal sulfide and sulfuric acidity, their decomposition temperature falls remarkably and decomposition reaction occurs quickly, and then explosives have the risk of the deflagration to the detonation transition. Heat resistant industrial explosives which can be used under condition of high temperature of 200°C and acidic environment were studied. We developed the explosive composition consisted of ammonium perchlorate as oxidizer saturated hydrocarbon oil as fuel and binder, and calcium carbonate as decomposition inhibitor. The characteristics of this explosive composition show the heat resistance over 24 hours at 200°C, and the detonation velocity over 2,500 m s<sup>-1</sup>. This explosive composition has a cap-sensitivity at temperature higher than 80°C.

### 1. Introduction

In some underground metal mine, the ground temperature rises remarkably with lowering site level, and the mining operation is conducted under the temperature higher than 100°C. It is not always sufficient to cool drift wall by means of the atomization of the cold water or the ventilation by the local fans. In the mine which contains the metal sulfide such as pyrites in ore, the explosives have the risk of sudden decomposition by the contact with pyrites under high temperature environment. It is considered that the decomposition of the oxidizer as the principal ingredient of explosive is promoted by the contact with pyrites.

The heat stability and reactivity of industrial explosives with pyrites were studied by some researchers<sup>1)~6)</sup>. They described that potassium oxalate, urea, zinc oxide, magnesium oxide, calcium carbonate, etc were found to be effective to prevent the reaction between the explosives and the pyrites. The emulsion explosive with heat resistance up to

160°C had been already developed in our laboratory, and had been used in some metal mine<sup>7)</sup>. Recently, the ground temperature of 200°C is confirmed by the prospecting in some metal mine. In blasting operation, the safety of the explosives is the highest priority. We started the study of the heat resistant industrial explosives which could be used under the condition of the high temperature of 200°C and the acidic environment.

For the heat resistant industrial explosives, it is necessary to have the high stability at high temperature. Preliminary examination was conducted about the stability of the explosive compounds such as RDX, HMX and HNS whose decomposition temperatures were 200°C or higher. It was found that when these explosive compounds were heated under acidic environment due to metal sulfide and sulfuric acidity, their decomposition temperature fell remarkably and decomposition reaction occurred quickly, and explosive compounds had the risk of the deflagration to the detonation transition. It was concluded that these explosive compounds could not be used as an ingredient of 200°C heat resistant industrial explosives. This investigation was carried out to improve the heat resistance performance of the emulsion explosive with heat resistance up to 160°C and to determine the explosive composition which contains

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ammonium perchlorate as principal ingredient.

## 2. Investigation of the emulsion explosive composition

### 2.1 Sample explosives

The emulsion explosive with heat resistance up to 160°C is mixed the powder of calcium carbonate with emulsion phase, that is emulsified from the oxidizing solution in which ammonium nitrate as a principal ingredient and thiourea are dissolved. Thiourea inhibits the decomposition reaction of explosive by trapping the active species such as N<sub>2</sub>O and NO<sub>2</sub> generated by decomposing the oxidizer. Previous paper<sup>8)</sup> described the decomposition inhibitory mechanism of calcium carbonate that the calcium ion, which mediates a hydroxide ion, must be adsorbed in the surface of pyrites. As a result, it is thought that the reaction of the oxidizer and pyrites is inhibited. The emulsion explosive with heat resistance up to 160 °C was made as a sample explosive I, and the composition with higher addition rate of the decomposition inhibitor, calcium carbonate, was made as a sample explosive II. The compositions of sample explosives are shown in Table 1.

Table 1 Compositions of sample explosives.

Sample explosives	Compositions
Base	Oxidizer 80wt%, Water 11wt%, Wax&Surface active agent 5wt%,GMB 4wt%
I	Base composition containing 1 wt% of thiourea and 7 wt% of calcium carbonate
II	Base composition containing 1 wt% of thiourea and 10 wt% of calcium carbonate

### 2.2 Heating test

The heating test was carried out to evaluate the heat stability of the sample explosives. Mine water containing pyrites generally shows the strong acidity attributed to the dissolution of the element of pyrites. That the mine water is concentrated under the high temperature, and strong acidity is formed. Its pH value is in the range of 2 to 3. When the explosive is used under such conditions, the explosive can contact with pyrites and mine water. It is very important to evaluate the heat stability of the explosive under such conditions, because

pyrites and mine water have the function to promote the decomposition of the explosive. The explosive, pyrites and mine water were completely mixed to imitate the severest situation, and the mixture was used as the sample for the heating test. Figure 1 shows the apparatus used for the heating test. The test sample was prepared by complete mixing 30g of the sample explosive, 30g of crushed pyrites and 5g of mine water, and that mixture was filled in test tube made of glass (30mm in the inside diameter). This test tube was set in steel tube (32mm in the inside diameter), and heated to 200°C with rubber heater that wrapped outside of steel tube. The temperature of the test sample was measured with the thermocouple, and the start of the decomposition of test sample was measured. The start of the decomposition was defined as decomposition delay time. The analysis of pyrites and mine water used for the heating test are shown in Table 2.

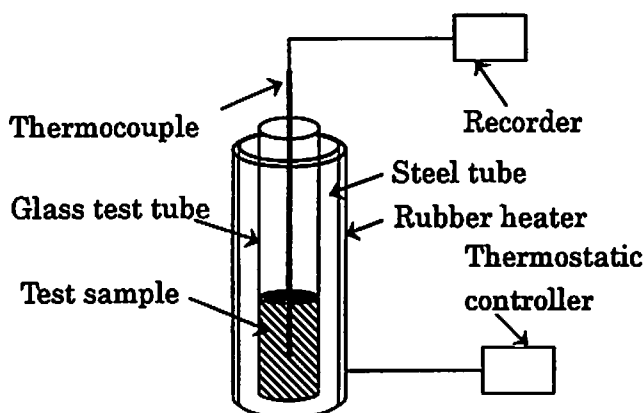


Fig. 1 Apparatus for heating test.

Table 2(a) Ingredients of pyrites.

Elements (%)							
Fe	S	Cu	Pb	Zn	Mn	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
43.85	48.86	0.10	0.27	0.68	0.10	2.95	0.30

Table 2(b) Ingredients of mine water.

Elements (mg l <sup>-1</sup> )							
Fe	Fe <sup>2+</sup>	Zn	Mn	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>
1216	565	1298	641	305	604	340	8860

### 2.3 Results and discussion

Figure 2 shows the relation between the decomposition delay time and temperature in the heating test of sample explosives I and II. It is known that ammonium nitrate used as the

oxidizer of the industrial explosive has the melting point at about 168°C, and its reactivity increases remarkably at the temperature higher than this melting point. It is considered that the emulsion explosive is much more resistant against heat decomposition than pure ammonium nitrate, because the oxidizer solution is covered with oil phase in the emulsion explosive. However, sample explosive I was decomposed in only three hours in the heating at 200°C. And even sample explosive II, which has a composition with the further addition of the decomposition inhibitor, was decomposed in five hours in the same condition. This result did not satisfy the target heat-resistance that the decomposition was not observed within 24 hours.

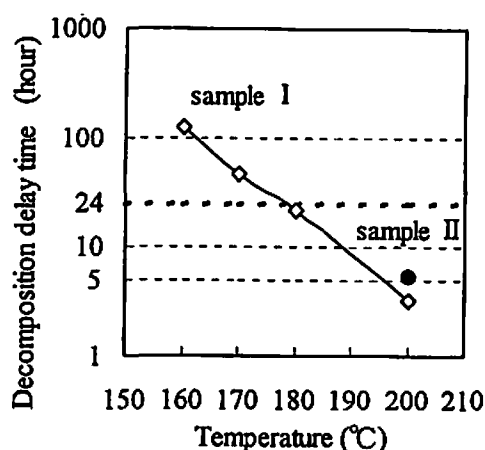


Fig. 2 The relation between decomposition delay time and temperature in heating test of sample explosives.

It was estimated that the improvement of heat resistance performance was not expected even if the further addition of decomposition inhibitor was conducted. Also, the stability of the emulsion structure might be degraded by further addition of decomposition inhibitor. It was concluded to be difficult to obtain heat resistance of 200°C using emulsion explosive.

### 3. Investigation of the explosive composition base on ammonium perchlorate

#### 3.1 Sample explosives

Judging from the above results, it was necessary for the explosive component to have the heat stability of 200°C. The composition based on

ammonium perchlorate (AP), that has higher heat stability than ammonium nitrate as oxidizer, was examined. However, it is known that the decomposition temperature falls remarkably under coexistence with pyrites, though AP has the heat stability of 200°C. Thus it is necessary to contain the decomposition inhibitor in the explosive composition. It was reported calcium carbonate and barium carbonate, etc. are effective as the decomposition inhibitor of AP<sup>9)</sup>. Calcium carbonate was selected as decomposition inhibitor because the heavy metal salt such as barium carbonate has a toxicity.

The sample explosives were prepared using AP as oxidizer, the content of each ingredient such as oil, decomposition inhibitor and density control agent was changed. The heat resistance and initiation sensitivity of these samples were compared, and the influences of each ingredient on the performance were investigated. The composition of sample explosives are shown in Table 3. The mixture ratio of AP and oil was adjusted to be 9:1 considering the dispersion condition of oil and oxygen balance. Also the hydrogenation refinement oil used in these compositions has high heat stability and the anti-oxidation property. Sample explosives were prepared according to the following purpose.

Sample A: Relation between grain size of AP and heat resistance.

Sample B: Relation between addition rate of calcium carbonate and heat resistance.

Sample C: Relation between grain size of AP and initiation sensitivity.

Table 3 Compositions of sample explosives.

Sample explosives	Compositions
Base	Ammonium perchlorate 90wt%, Oil 10wt% (base composition)
A	Base composition containing 8 wt% of calcium carbonate
B	Base composition containing 8-30 wt% of calcium carbonate
C	Base composition containing 8 wt% of calcium carbonate and 3 wt% GMB
D	Base composition containing 8-40 wt% of calcium carbonate and 3 wt% GMB
E	Base composition containing 30 wt% of calcium carbonate and 0.7 wt% GMB

Sample D: Relation between addition rate of calcium carbonate and initiation sensitivity.

Sample E: Relation between bulk density of explosive and explosion performance.

### 3.2 Thermal analysis

The thermal analysis test was performed by means of DSC (differential scanning calorimeter) to study the influence of grain size on heat stability of AP. The DSC apparatus used was Seiko Instruments Inc. DSC200. The measurements were carried out for AP of 10, 35, and 200 $\mu\text{m}$  in diameter respectively. The measurements were performed using sealed stainless cell and setting the gradient temperature of 10K  $\text{min}^{-1}$ .

### 3.3 Heating test

The heating test was conducted with the same method for the investigation of the sample emulsion explosives.

### 3.4 Initiation test

The initiation test was carried out to evaluate the cap sensitivity of the explosives under the high temperature environment. The sample explosive was charged in silicon tube (32mm in the inside diameter), and the opening of the tube was sealed with silicon rubber plug. This set-up was heated to 150 $^{\circ}\text{C}$  in the thermostatic chamber. Five hours later, it was set in steel tube (42mm in the inside diameter), and the sample explosive was initiated by a heat resistance electric detonator at 150 $^{\circ}\text{C}$  to investigate the detonability. Moreover, the detonation velocity of the sample was measured by the ionized gap method.

### 3.5 Results and discussion

#### 3.5.1 Thermal analysis

The chart of DSC of AP in each grain size is shown in Fig. 3. After the phase transition from diagonal to cubic at about 240 $^{\circ}\text{C}$ , pyrolysis of AP appears separately on two stages. One is the low

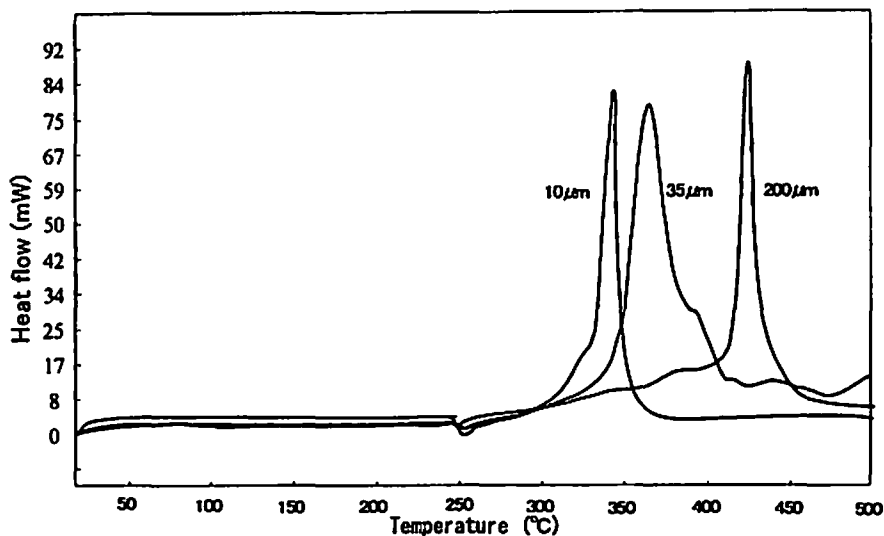


Fig. 3 The chart of DSC of ammonium perchlorate.

temperature decomposition area at about 250 $^{\circ}\text{C}$ , and the other is the high temperature decomposition area at about 350 $^{\circ}\text{C}$ . About the pyrolysis of AP, it is shown that the decomposition temperature at the high temperature area shifts to lower temperature side as the grain size becomes smaller, while the grain size does not influence on the decomposition temperature at the low temperature area<sup>10)</sup>. It was confirmed in our analysis that the low temperature decomposition in each grain size was observed at about 250 $^{\circ}\text{C}$ ,

and the high temperature decomposition shifted to the lower temperature side as the grain size became smaller.

#### 3.5.2 Heating test

The result of the heating test for sample explosive A is shown in Table 4. As shown in Table 4, the sample explosive prepared using AP with small grain size presented the lower heat stability. It is thought that the decomposition reaction is promoted because AP contact with pyrites on large

area. The relation between the content of calcium carbonate and the decomposition delay time at 200 °C is described in Fig. 4. This investigation was

Table 4 Result of heating test for sample explosive A.

Average diameter of AP	35 $\mu$ m	400 $\mu$ m
Decomposition delay time	2.3 hour	5 hour
State of decomposition	DDT	Decomposition

carried out using the sample explosive B in which the content of calcium carbonate was varied. It becomes clear that the addition of 28% or more of calcium carbonate is necessary to obtain heat stability for over 24 hours at 200°C as shown in Fig. 4. The decomposition inhibitory mechanism

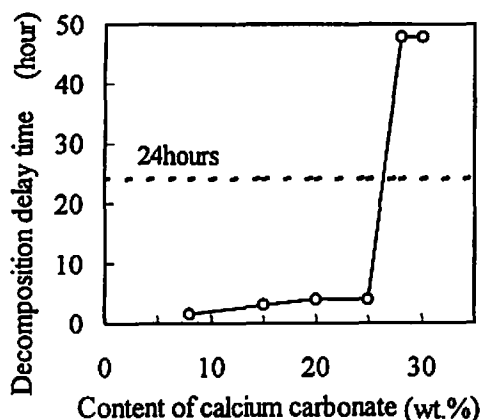


Fig. 4 The relation between content of calcium carbonate and decomposition delay time at 200°C.

of AP by the calcium carbonate was studied<sup>11)</sup>. The species of  $\text{ClO}_4^-$  and  $\text{ClO}_2^-$  generate in the early period of the decomposition reaction of AP, and promote its reaction as the active species. Calcium carbonate decreases the active species and inhibits the decomposition reaction by bonding with these active species. Furthermore,  $\text{Ca}(\text{ClO}_4)_2/\text{CaCl}_2$  that has the higher heat stability than AP is formed by bonding with calcium carbonate and the active species, and the decomposition rate is decelerated. It is assumed that the difference on decomposition reaction in Table 4 due to the size of the grain size of AP used in sample A is attributed to the progress of the self catalytic reaction. In other words, small grain size of AP can generate large amount of active species in the early period of the decomposition reaction, and self catalytic reaction which accelerates the decomposition reaction is

promoted by reaction heat.

### 3.5.3 Initiation test

The results of the initiation test for sample explosive C is shown in Table 5. In the sample explosives using AP of single grain size, the sample explosive with smaller grain size demonstrated the higher initiation sensitivity. Also, in the sample explosives which including AP of two grain size, the sample explosive with high ratio of small grain size demonstrated the higher initiation sensitivity. Accordingly, it is clear that the initiation sensitivity depends on the grain size of AP.

Table 5 Result of the initiation test for sample explosive C.

Ratio of mix	Density ( $\text{g cm}^{-3}$ )	Results
35 $\mu$ m-100%	0.85	Detonation
200 $\mu$ m-100%	1.09	Non-detonation
400 $\mu$ m-100%	1.03	Non-detonation
35 $\mu$ m:200 $\mu$ m = 50%:50%	1.00	Detonation
35 $\mu$ m:200 $\mu$ m = 20%:80%	1.05	Non-detonation
35 $\mu$ m:400 $\mu$ m = 50%:50%	1.03	Detonation
35 $\mu$ m:200 $\mu$ m = 20%:80%	1.07	Non-detonation

The results of the initiation test for sample explosive D are shown in Table 6. Calcium carbonate is expected to decrease the initiation sensitivity of the explosives with the increase of the addition rate, because it is the inert substance which does not contribute to the detonation reaction, although it is effective as the decomposition inhibitor of AP. Thus, it is necessary to confirm the addition rate to satisfy both the heat stability and the initiation sensitivity of explosive at 200°C. As for the addition rate of calcium carbonate, it is concluded that the range of 28-30% is the best ratio judging from the results in Fig. 4 (sample explosive B) and Table 6.

The results of the initiation test and measurements of detonation velocity of sample explosive E are shown in Fig. 5. AP needs the addition of density control agent such as glass microballoon (GMB), because AP has lower reactivity than explosive compounds such as RDX. It may be stated that GMB are necessary, because the sample explosive without GMB can not be

Table 6 Result of the initiation test for sample explosive D.

Content of calcium carbonate (wt%)	Density (g cm <sup>-3</sup> )	Results
8	0.85	Detonation
13	0.90	Detonation
20	0.87	Detonation
30	0.95	Detonation
40	1.00	Non-detonation

initiated as shown in Fig. 5. The detonation velocity attains its maximum at fewest addition rate of GMB. The steel tubes after the initiation test are

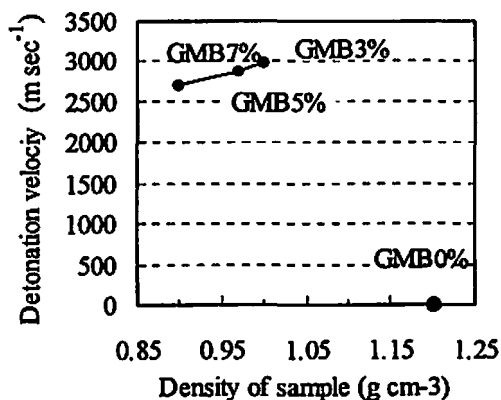


Fig. 5 The relation between density of sample and detonation velocity.

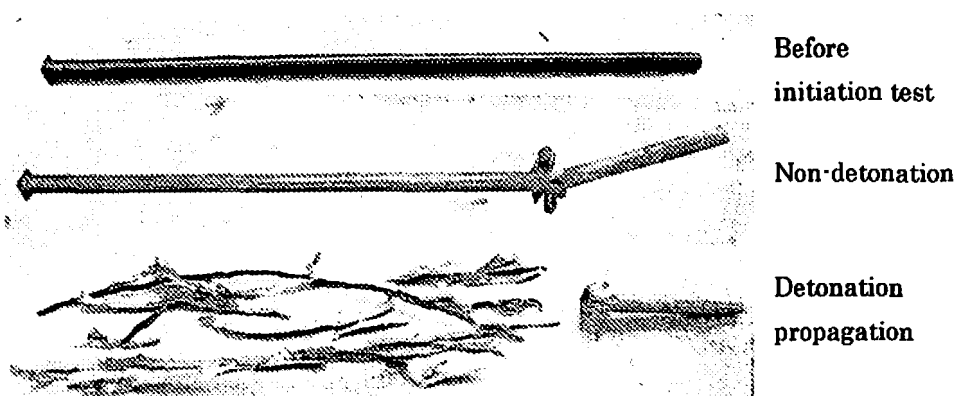


Fig. 6 Steel tube after the initiation test.

shown in Fig. 6. The steel tube was greatly destroyed in the case of the detonation propagation, but the destruction of the steel tube was observed at small portion in the case of the non-detonation because only the sample explosive around detonator reacted. Figure 7 shows the relation between the diameter of explosive and detonation velocity in sample explosive E. It is shown that the detonation velocity increases with the increase of diameter of sample explosive. The measured detonation velocity is much lower than the ideal detonation velocity of 4600 m s<sup>-1</sup> calculated using KHT equation of state, which indicates non-ideal detonation behavior of AP based explosive composition. The relation between the temperature and the initiation sensitivity for sample explosive E is shown in Table 7. The temperature sensitivity is very low so that the sample explosive can not detonate less than 80°C. However, this is not a problem taking account of the actual environment

in which this explosive is used. Contrary, this fact shows rather high safety for the handling of AP based explosive composition.

#### 4. Conclusions

As a result of the investigation of the heat

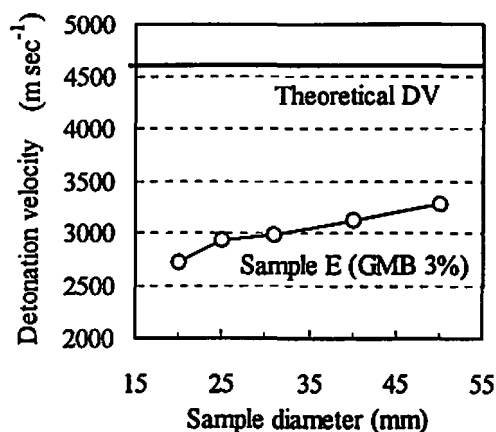


Fig. 7 The relation between sample diameter and detonation velocity.

**Table 7 Relation between the temperature and the initiation sensitivity for sample explosive E.**

	Explosive temperature		
	20°C	50°C	80°C
Sample E (GMB 3%)	Non- detonation	Non- detonation	Detonation

resistant industrial explosives which can be used at high temperature of 200°C even in acidic environment, the following conclusions were obtained.

- (1) It was found that the emulsion explosive, whose principal ingredient was ammonium nitrate, was not able to inhibit the decomposition, even when sufficient decomposition inhibitor was added under the high temperature environment which exceeded the melting point of ammonium nitrate.
- (2) Heat resistance over 24 hours at 200°C was obtained by adding calcium carbonate to the explosive using AP as oxidizer under coexistence with the decomposition promoter such as pyrites.

#### References

- 1) D.R.Forshey, T.C.Ruhe, C.M.Mason, Mining Congress Journal, 55(1), 34-35 (1969)
- 2) Yael Miron, T.C.Ruhe, W.Watson, Bureau of Mines Report of Investigations, 837 (1979)
- 3) Y.Ikeda, Y.Tanabe, A.Inoue, and K.Yamamoto, J.Ind.Explos.Soc.,Japan, 45, 234-239 (1984)
- 4) S.Sato, I.Tsubaki, and T.Suenaga, J.Ind.Explos.Soc., Japan, 38, 286-288 (1977)
- 5) S.Matsumoto, and M.Tanaka, Mining and Safety, 31, 1-7 (1985)
- 6) Y.Shimomura, and H.Sakai, J.Ind.Explos.Soc., Japan, 23, 111-119 (1962)
- 7) T.Sawada, K.Kurokawa, F.Sumiya, and Y.Kato, J.Ind.Explos.Soc.,Japan, 53, 212-218 (1992)
- 8) T.Sai, I.Matsuoka, and J.Shimoiizaka, Journal of the Mining and Metallurgical Institute of Japan, 87, 1053-1057 (1987)
- 9) A.E.Simchen and Livia Inbar-Rozem, Israel Journal of Chemistry, 6, 937-948 (1968)
- 10) H.Osada, E.Sakamoto, J.Ind.Explos.Soc., Japan, 24, 236-244 (1963)
- 11) R.P.Rastogi, Gurdip Singh and Ram Raj Singh, J.Appl.Chem.Biotechnol, 28, 889-894 (1978)