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# Stabilization effects of carboxylate on pyrotechnic compositions including Mg powder in water

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**Abstract**

Magnesium powder is a common fuel in the field of pyrotechnics. The metal corrodes easily under wet conditions. This can lead to problems such as spontaneous ignition and deterioration of combustion performance when the powder is used in humid areas. For pyrotechnic compositions containing magnesium, harmful stabilizers are often used. In this study, we researched a less harmful replacement for the stabilizer and selected linseed oil, which is used as cooking oil. Experiments were conducted to examine linseed oil's stabilization effects against magnesium corrosion when it is in contact with an oxidizer under humid conditions by coating magnesium powder and soaking it in aqueous oxidizer solutions. The oxidation of linseed oil led to its polymerization, because of which the stabilizing effect of linseed oil was lost. Stearic acid, which is a saturated fatty acid, was also examined for its stabilizing effects. Melted stearic acid was mixed with magnesium and coating of stearic acid on magnesium particles was confirmed. The effect of stearic acid coating is more prominent than that of simple mixing of stearic acid with Mg. The stabilization effect of linseed oil and stearic acid coating shows that unharmful organic stabilizers can also be used in pyrotechnic compositions containing Mg.

**Keywords:** Pyrotechnics, Magnesium, Corrosion, Isothermal calorimeter, Stabilizer

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## 1. Introduction

Magnesium powder is a conventional fuel for explosives because its combustion provides large amounts of energy and high brightness, which is favorable for pyrotechnics. Meanwhile, pyrotechnic compositions that include magnesium powder have corrosion problems [1-10]. The corrosion of magnesium is accelerated by it is mixed with oxidizers in pyrotechnics. Such corrosion can lead to spontaneous ignition or quality deterioration. Thus, stabilization against the corrosion is important for further use of magnesium powder in pyrotechnics.

To prevent corrosion, stabilizers are added to magnesium powder in the pyrotechnic composition. Chromate salts have been used in fireworks because of their stabilization effect against magnesium corrosion [13]. However, it is harmful to the human body and environment [11-12]; therefore, in this study, less harmful stabilization methods against magnesium powder corrosion are researched.

Stabilizers without chromate salts had also been investigated. It is reported that polymer coating with Elvax could prevent the corrosion of Mg in pyrotechnics [1], but the coating process required organic solvent which is harmful for humans and has hazard of fire. In another report, boric acid was tested as a stabilizer in pyrotechnics, but it is not appropriate for the one containing Mg [13-14].

Linseed oil was also used as an organic stabilizer to prevent corrosion [15]. It is obtained from the seed of the flax plant, and its main components are the glycerides of linolenic acid, linoleic acid, and oleic acid. These are unsaturated aliphatic carboxylates that consist of 18 carbon atoms [16]. Linseed oil is sometimes used as cooking oil. In pyrotechnics, the oil is usually mixed with other materials to prevent contact with water. Linseed oil can be oxidized and polymerizes via peroxide, and the oxidation progresses easily [17]. Linseed oil oxidation can cause performance loss during storage or transportation; however, the polymerized products are suitable for use as solid coatings on pyrotechnic compositions. Therefore, it has been used in the fireworks industry after deliberate oxidation [13]. However, it has previously been reported that coating with oxidized linseed oil does not work well in solutions containing ammonium perchlorate because the coating comes off in solution [3]. Using raw linseed oil as a stabilizer would simplify the pyrotechnic manufacturing process, but its ability to prevent oxidation has not been previously studied.

In this paper, we aimed to measure the stabilization effects of linseed oil against the reaction between magnesium and oxidizer solutions by using a calorimeter. In addition, stearic acid was studied for its potential stabilizing effect.

## 2. Experiments

### 2.1 Sample preparation

Magnesium (Mg) powder (Kanto Metal Corporation.; purity > 99.9%) was used as magnesium samples. Ammonium perchlorate (AP) (Wako Pure Chemical Industries, Ltd.; G.R.) and ammonium nitrate (AN) (Wako Pure Chemical Industries, Ltd.; G.R.) were used as oxidizers. Raw linseed oil (LO(R)) (Wako Pure Chemical Industries, Ltd.; E.P.), stearic acid (HSt) (also called octadecanoic acid, Wako Pure Chemical Industries, Ltd.; G.R.), magnesium stearate (MgSt) (Sigma-Aldrich; E.P.), and potassium dichromate (PD) (Wako Pure Chemical Industries, Ltd.; G.R.) were chosen as additives. The magnesium powder was passed through a 100-mesh screen, and the particles collected on a 140-mesh screen were used in this study. Thus, the particle size of Mg powder is 106–150 μm. This powder was separated into 106–150 μm and 75–106 μm particles through sieves. Since fine

Mg is highly reactive, Mg powder of this size were used for the experiments.

Oxidized linseed oil (LO(O)) was obtained by heating LO(R). LO(R) was heated on a watch glass in a thermostatic oven for 20 h at 80 °C. The LO(O) preparation conditions were determined based on the accelerated oxidation test in a previous study [17]. Mg-LO(R) and Mg-LO(O) were prepared by mixing Mg and unoxidized or oxidized linseed oil in a glass vessel before carrying out measurements in an isothermal calorimeter.

Coated magnesium powder was prepared with melted stearic acid. Stearic acid powder and magnesium powder were mixed in a glass cup. The cup was heated with hot water to over 80 °C, which is beyond melting point of stearic acid [18]. The wt. ratio of magnesium powder to stearic acid was 5/1. The product is henceforth referred as Mg(HSt).

Aqueous solutions of 1 mol $L^{-1}$ AP and 1 mol $L^{-1}$ AN were prepared in a 50 mL measuring flask. Deionized water was used to dilute the oxidizers. Additives were mixed to 1 mmol Mg to simulate actual firework composition (the wt. ratio of Mg to additives is 5/1) [13]. 1 mmol of Mg powder in a glass vessel was placed in a calorimeter, and then, 2 ml of oxidizer solution was added to it. In this composition, about 4.9 mg of the additives (LO(R), LO(O), HSt, PD) were present in 2 ml of the oxidizer solution.

## 2.2 Isothermal calorimeter

A schematic view of the isothermal calorimeter is shown in Fig1.

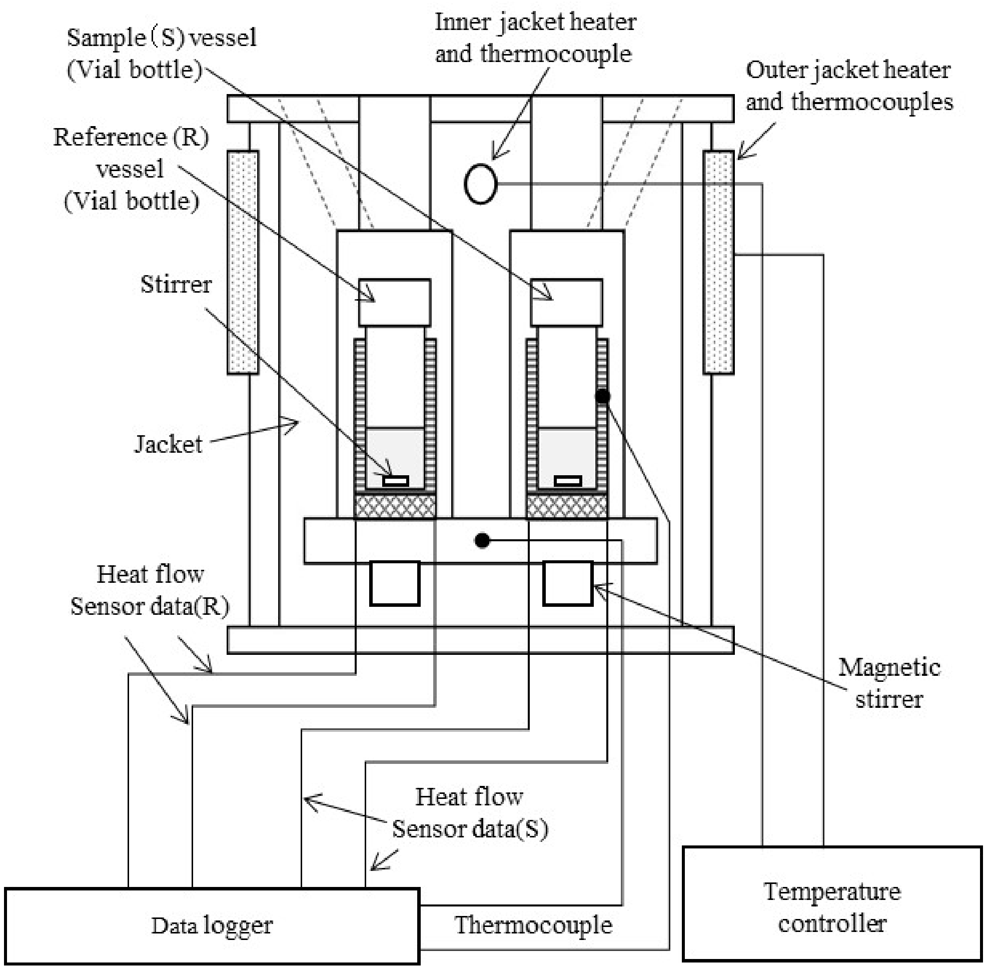

**Fig. 1** Isothermal calorimeter schematic

Heat generation was monitored with an isothermal calorimeter (Fig1). The reaction was carried out at 25 °C, and the stirring rate was about 10 revolutions per second. All reactions were measured for 100 min, and each sample was observed over 3 times. The heat flow sensor data (Reference) was subtracted from the heat sensor data (Sample). The time constant was 5.28 min. The generated heat was normalized by the weight of magnesium in the reaction.

The rate-of-stabilization effect was calculated by comparing the heat generated during the reaction with the oxidizer in water (oxidizer/samples). The stabilization rates ($\eta$) against Mg -oxidizer reaction were calculated using the following equation;

$$\eta = 100 - 100 \times Q_{\mathrm{peak}}\ (\mathrm{AP\ or\ AN/Mg\text{-}Additives})/Q_{\mathrm{peak}}\ (\mathrm{AP\ or\ AN/Mg}). \quad (1)$$

$Q_{\mathrm{peak}}$ is the heat generated during the reaction until the reaction rate reached a maximum value, and Mg-Additives means the weight of Mg mixed with additives.

### 2.3 Analysis of coating on Mg

The coated Mg powder was observed by scanning electron microscopy (SEM) under high vacuum conditions at 15 kV acceleration voltage, using a JSM-7001F (JEOL Ltd.) scanning electron microscope.

The composition of the coated Mg was identified by powder X-ray diffraction analysis (XRD), using a SmartLab X-Ray diffractometer (Rigaku Corporation). Cu Kα radiation was used at 40 kV and 50 mA, while the scanning speed was 10° min$^{-1}$ in the XRD.

## 3. Results and discussion

### 3.1 Stabilization effects of linseed oil

In the calorimetric experiments, LO(R) showed stabilizing effects against the reaction between Mg and the oxidizer in aqueous solutions of AP and AN. Fig 2 and Table 1 show that the effect of LO(R) is to reduce the heat generation between magnesium and the oxidizer solution.

Unlike LO(R), LO(O) did not show a clear stabilization effect, as is indicated in Fig 2 and Table 1. These results indicate that the oxidization of LO(R) decreased the stabilization effects, consistent with the findings of a previous study [3], which described the loss of stabilization due to LO polymerization and caking after heating.

The stabilization effects of carboxylate salts have been previously studied and reported [19-20]. A stabilization mechanism of straight-chain in aliphatic carboxylate was proposed [20]. When hydrophilic groups in carboxylate salts adsorb on the magnesium surface, the hydrophobic groups face outward and repel water. Hydrophobic groups are also found in the ingredients of linseed oil. Therefore, linseed oil is expected to work as stabilizer. Based on the experimental result, LO(R) was proven to produce a stabilizing effect due to the straight-carbon chain, which was lost by LO(R) polymerization.

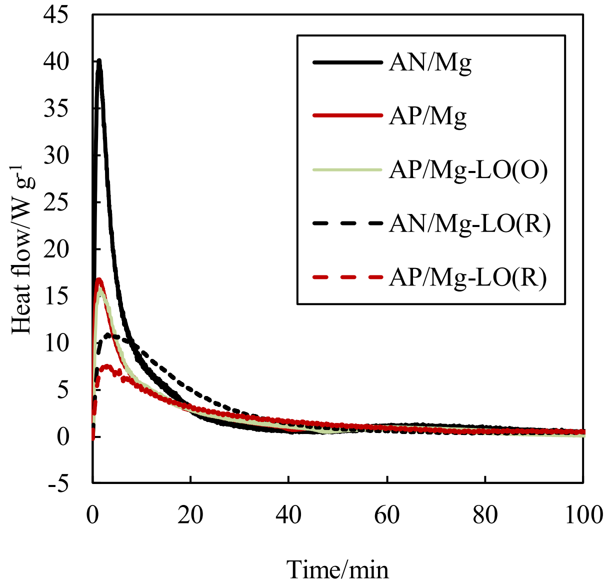


**Fig. 2** Results of isothermal calorimetry. AN/Mg means mixture of AN(Ammonium nitrate aqueous solution) and Mg(Magnesium powder). AP/Mg means mixture of AP (Ammonium perchlorate aqueous solution) and Mg. Mg-LO(O) means mixture of Mg and heated linseed oil. Mg-LO(R) means mixture of Mg and raw linseed oil

Table 1 Analysis results of isothermal calorimetry.
Average time to peak tops (AP/Mg: 1.32 min, AN/Mg: 1.18 min)
AN (Ammonium nitrate), AP (Ammonium perchlorate), Mg (Magnesium),
LO(O) (Oxidized linseed oil), LO(R) (Raw linseed oil).
$Q$ is heat generation and $\eta$ is rate of stabilization

| Oxidizer | Fuel | $Q_{peak}$ /kJ g$^{-1}$ | $Q_{100\ min}$ /kJ g$^{-1}$ | $\eta$/% |
|---|---|---|---|---|
| AN | Mg | 1.83 | 19.2 | - |
| | Mg-LO(R) | 0.394 | 14.7 | 78.6 |
| AP | Mg | 1.18 | 13.9 | - |
| | Mg-LO(R) | 0.289 | 12.2 | 75.5 |
| | Mg-LO(O) | 1.04 | 12.3 | 11.7 |

3.2 Stabilization effects of stearic acid

Stearic acid (HSt) is a C18 carboxylic acid similar to the other components of linseed oil but without unsaturated bonds [21]. Based on the experimental results of LO(R), HSt was selected as a potential candidate for stabilizer, and its stabilizing effects against the reaction between Mg and the oxidizer were evaluated. In this study, HSt was melted to coat (Mg(HSt)). HSt is solid at room temperature and it cannot cover Mg well under dry conditions.

Fig 3 shows the difference of surface conditions between Mg and Mg(HSt). The surface of Mg(HSt) was smoother than that of Mg powder. The change in the surface area decreases the rate of reaction between Mg and the oxidizer in solution.

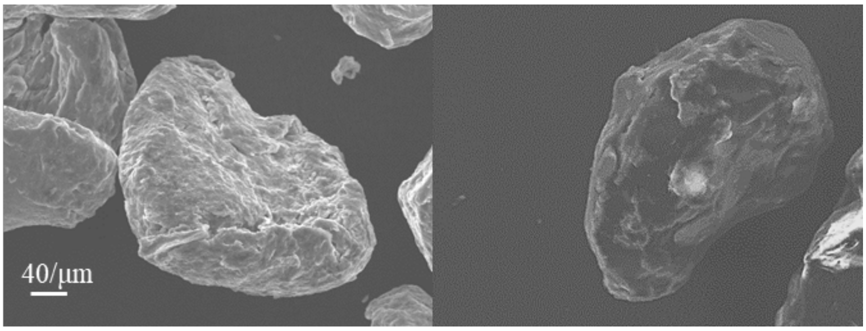


**Fig. 3** Comparison of SEM results between reagents of magnesium powder ((Mg) : Left) and coated magnesium with stearic acid (Mg(HSt): Right)

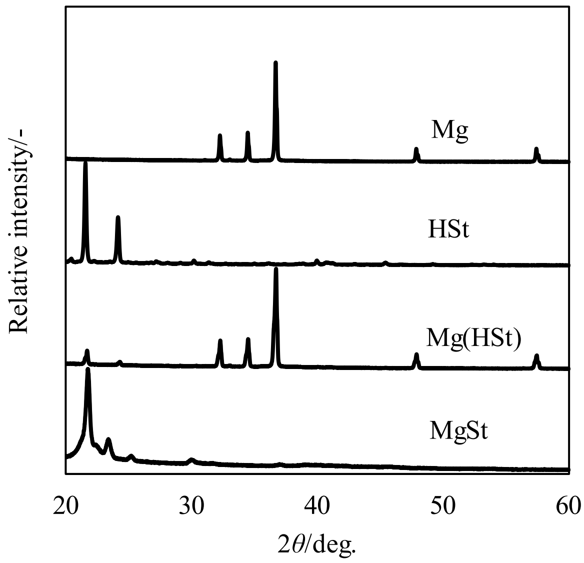


**Fig. 4** XRD results of Coated Mg (Mg(HSt))

Mg means magnesium powder and HSt means stearic acid, MgSt means magnesium stearate. Mg(HSt) means magnesium which is coated with stearic acid.

The XRD analysis (Fig 4) showed that the main component on the Mg surface was HSt. The reaction of Mg and HSt during coating process was suspected, and MgSt may have been generated. However, no peaks corresponding to MgSt were found in the XRD spectrum of Mg(HSt).

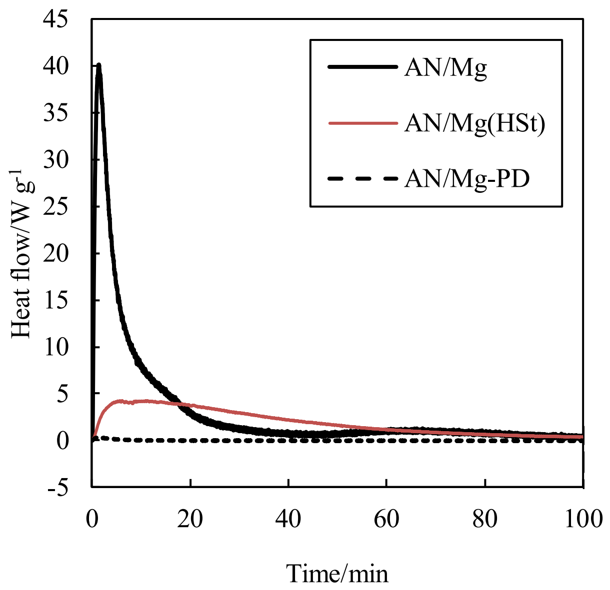


**Fig. 5** Results of isothermal calorimetry. AN/Mg means mixture of AN(Ammonium nitrate aqueous solution) and Mg(Magnesium powder). Mg(HSt) means Mg powder which is coated with stearic acid. Mg-PD means mixture of Mg and potassium dichromate.

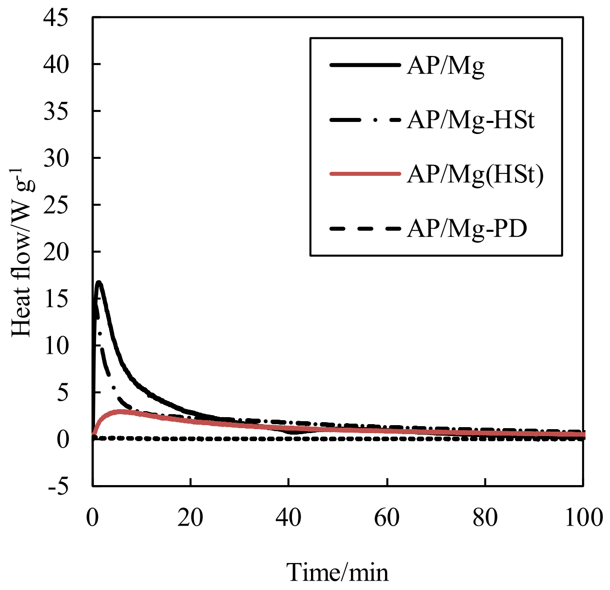


**Fig. 6** Results of isothermal calorimetry. AP/Mg means mixture of AP (Ammonium perchlorate aqueous solution) and Mg (Magnesium powder). Mg-HSt means mixture of Mg and stearic acid. Mg(HSt) means Mg powder which is coated with stearic acid. Mg-PD means mixture of Mg and potassium dichromate

Table 2 Analysis results of isothermal calorimetry.
Average time to peak tops (AP/Mg: 1.32 min, AN/Mg: 1.18 min)
AN (Ammonium nitrate), AP (Ammonium perchlorate), Mg (Magnesium), HSt (Stearic acid), Mg(HSt) (Magnesium powder which is coated with stearic acid), PD (Potassium dichromate).
$Q$ is heat generation and $\eta$ is rate of stabilization

| Oxidizer | Fuel | $Q_{peak}$ /kJ g$^{-1}$ | $Q_{100\ min}$ /kJ g$^{-1}$ | $\eta$ % |
|---|---|---|---|---|
| AN | Mg | 1.84 | 19.2 | - |
| | Mg(HSt) | 0.136 | 11.3 | 92.6 |
| | Mg-PD | 0.0157 | 0.140 | 99.1 |
| AP | Mg | 1,18 | 13.9 | - |
| | Mg-HSt | 0.946 | 11.8 | 19.9 |
| | Mg(HSt) | 0.125 | 8.52 | 89.4 |
| | Mg-PD | 0.0530 | 0.360 | 95.5 |

Stabilization effects of HSt and PD are shown in Fig 5, Fig 6, and Table 2. The results from AP/Mg(HSt) and AN/Mg(HSt) show that HSt produces greater stabilization effects than LO(R).

The comparison between Mg coated with HSt (AP/Mg(HSt)) and Mg mixed with HSt powder (AP/Mg-HSt) indicated that the coating process increased the stabilization effect. The difference can be explained by the large difference in heat generation between AP/Mg(HSt) and AP/Mg-HSt. The $\eta$ of HSt coating was about 90%. These results show that coating with HSt worked as a method to stabilize Mg against the reaction with water resulting in corrosion.

The stabilization of HSt coating is more effective along the duration of this experiment than the polymer coating which was reported in a previous investigation [1]. However, HSt coating was less effective at preventing corrosion than PD, as shown in Fig 5, Fig 6 and Table 2.

**4. Conclusion**

Our investigation revealed that law linseed oil has a stabilizing effect against the reaction between Mg and the oxidizer in aqueous solutions of AP and AN. However, the oxidization of LO(R) reduces its stabilization effect after polymerization.

Selection of a saturated aliphatic compound such as stearic acid is important for solving the problem of polymerization. Our experiments revealed that stearic acid coating exhibited better stabilizing than LO(R).

The stabilization effect of the stearic acid coating was smaller than PD, which is a conventional stabilizer. However, PD is harmful to the human body and environment, and people in the pyrotechnic industry have been exposed to it. Therefore, an unharmful stabilizer is desired, and carboxylate can be a potential stabilizer. Saturated aliphatic carboxylate is a suitable stabilizer because it can circumvent the polymerization step, which was inevitable in the case of linseed oil. In order to use the carboxylate as a stabilizer, it is necessary to measure the stabilization effect in the long term, because stabilization with polymer in the previous report was tested for long term.

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