Effect of magnesium stearate coating on degradation of NH4ClO4/Mg by moisture

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1 Introduction

Degradation of various compositions by moisture persists as one of the serious problems in the field of energetic materials [1]-[8]. In particular, pyrotechnic compositions containing magnesium (Mg) powder are degraded easily by water [9]. Since Mg is used in many pyrotechnics such as flares and fireworks, it is essential to prevent its degradation to create a strong light emission during combustion. Although potassium dichromate (PD) has been used as an effective stabilizer for a long time to solve this problem [9], it is harmful for human health and environment [10][11]. Hence, pyrotechnic compositions containing Mg require an alternative stabilizer for safer use.

Previous investigations on structural materials revealed that carboxylate salts could work as stabilizers as their hydrophobic groups could repel water on the metal surface [12]-[14].

Inspired by this, magnesium stearate (MgSt), which has an analogous hydrophobic group, is chosen as potential stabilizer in this study. The extent of its stabilization effect against degradation by moisture is measured in a pyrotechnic composition comprising ammonium perchlorate (AP) and Mg.

In addition to preventing degradation, the effects of this stabilizer on the burning rate and flame color were also studied in the burning test, since combustion performances in pyrotechnics could not be neglected.

2 Experimental Section

2.1 Sample preparation

Mg (Kanto Metal Corporation; purity > 99.9%), MgSt (Sigma-Aldrich; E.P.), PD (Wako Pure Chemical Industries, Ltd.; G.R.), stearic acid (HSt) (Wako Pure Chemical Industries, Ltd.; G.R.), calcium stearate (CaSt) (Sigma-Aldrich; C.P.), AP (Wako Pure Chemical Industries, Ltd.; G.R.), and hydroxyl-terminated polybutadiene (HTPB) (Idemitsu Kosan Co., Ltd.; Poly bd™ R-15HT (hydroxyl group content; 1.84 mol/kg)) were purchased and used without further purification. Mg particles that passed through a 100-mesh screen and got collected on a 140-mesh screen were used.

Mg coated with potential stabilizers MgSt, PD, HSt, and CaSt was prepared for aging and burning tests. Each stabilizer was added to water in a separate glass cup and Mg was mixed with stabilizer in water at room temperature. The mixture of Mg/stabilizer contained one parts by weight of stabilizer and 5 parts by weight of Mg, which was determined based on the composition of fireworks [9]. And one part by weight of water was added to one part by weight of Mg. After mixing, each cup was stored at room temperature in sealed vessels containing silica gel and dried for over 12 h. Hereinafter, the dried samples, which are Mg coated with MgSt, PD, HSt, CaSt, are referred to as Mg(MgSt), Mg(PD), Mg(HSt), Mg(CaSt), respectively.

Table 1. Parts by weight of samples for burning test.

No.	Sample name	Parts by weight [-]						Condition of stabilizer
		Main composition			Sutabilizer			
		AP	HTPB	Mg	MgSt	HSt	CaSt	
1	AP/HTPB/Mg(MgSt)	24	6	5	1	-	-	Covered on Mg
2	AP/HTPB/Mg(HSt)	24	6	5	-	1	-	Covered on Mg
3	AP/HTPB/Mg(CaSt)	24	6	5	-	-	1	Covered on Mg
4	AP/HTPB/Mg/MgSt	24	6	5	1	-	-	Mixed with Mg
5	AP/HTPB/Mg	24	6	5	-	-	-	–

For aging test, AP/Mg, AP/Mg(MgSt), and AP/Mg(PD) were prepared. These mixture consisted of 12 parts by weight of AP and 5 parts by weight of Mg or 6 parts by weight of Mg(Stabilizer), which was based on the composition of fireworks [9]. The mixtures were set on plastic cups before aging test.

For burning test, samples (about 2.2 g) filled into stainless tubes (diameter: 5 mm, length: 50 mm) were prepared. HTPB was added to ensure safety in the mixing process. The parts by weight of AP, Mg were different from ones in aging test for the sake of addition of HTPB. The parts by weight of chemicals are shown in table 1. The effects of coating with other stearates, HSt and CaSt, on the burning rate were observed as well. For comparison, a reference sample was prepared in which MgSt powder was simply mixed with Mg.

2.2 Aging test

Aging test was carried out by storing samples (20 mg) in a plastic container, which was placed in an incubator at a constant temperature (40 °C) and humidity (75% RH). humidity was kept with sodium chloride (NaCl) (Wako Pure Chemical Industries, Ltd.; E.P.), following the saturated salt method [15]. After storing for 24 h, each sample was dried for 1 h under vacuum. The weights of the samples were measured before and after aging test for comparing the degradation progress. A chemical reaction between Mg and H_2O results in degradation products, which increases the weight of the samples [16].

2.3 Powder X-ray diffraction

Samples were analyzed by powder X-ray diffraction (XRD) before and after the aging test. SmartLab X-ray diffractometer (Rigaku Corporation) was used for XRD analysis. The Cu Kα radiation was used at 40 kV and 50 mA, while the scanning speed was 5° min^{-1}. PDXL2 software (Rigaku Corporation) was used for the analysis of XRD patterns. Since the degradation of AP/Mg by moisture results in $Mg(OH)_2$ [16], this experiment focused on the peaks that are particularly derived from $Mg(OH)_2$.

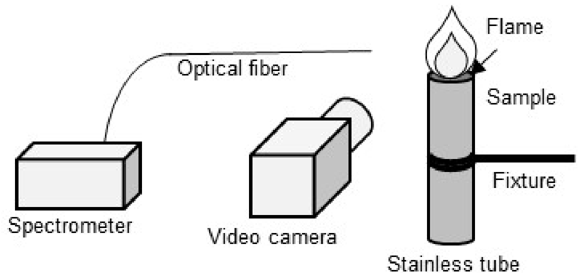

Figure 1. Schematic view of the burning test.

2.4 Burning test

A schematic view of the burning test is shown in Figure 1. Sample filled tubes were ignited on the top by a gas torch at ambient temperature. The burning times were measured by video camera recording, and the burning rate was calculated from burning time and sample length. Burning time is defined as the time from ignition to extinction of flame. Since the color of flame is an important parameter in pyrotechnics, flame spectrum was measured by spectrometer HR-4000 (Ocean Optics Inc.). Integration time of the spectrometer was 200 ms, and all spectra were obtained in the wavelength range of 400–1000 nm. Samples AP/HTPB/Mg and AP/HTPB/Mg(MgSt) were used to compare the effect of coating, while samples AP/HTPB/Mg(MgSt), AP/HTPB/Mg(HSt), and AP/HTPB/Mg(CaSt) were used to compare the effect of the stabilizer.

3 Results and Discussion

3.1 Aging test

The XRD spectra of Mg, Mg(MgSt), and Mg(PD) before the aging test are shown in Figure 2. Mg(MgSt) shows the diffraction pattern derived from MgSt and Mg, while Mg(PD) shows peaks derived from PD. Figure 2 indicates that the stabilizers were unchanged before the aging process. Although the coating process on Mg was conducted in water and the process could generate $Mg(OH)_2$, the XRD patterns showed no peaks derived from $Mg(OH)_2$. The sample exhibited no evidence of deterioration because of the coating.

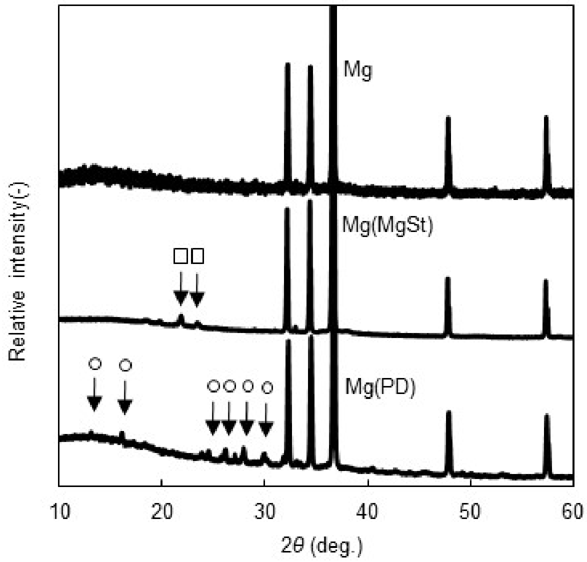

Figure 2. XRD curves of Mg, Mg(MgSt) and Mg(PD).

(□: Derived from MgSt, ○: Derived from PD)

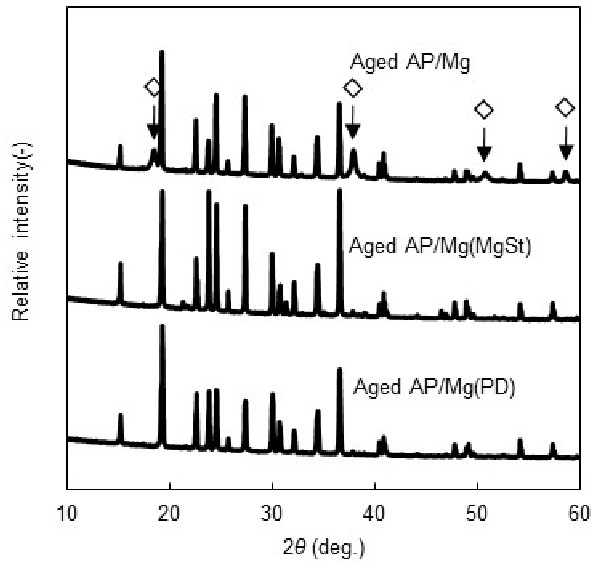

Figure 3. XRD curves of samples after aging test.

(◇: Derived from $Mg(OH)_2$)

The results of XRD analysis after aging test are shown in Figure 3. AP/Mg shows the pattern derived from the degradation product, $Mg(OH)_2$. The XRD patterns of aged AP/Mg(MgSt) and AP/Mg(PD) did not show the $Mg(OH)_2$ peaks clearly. This phenomenon indicates that coating with MgSt and PD prevented the generation of $Mg(OH)_2$.

Figure 4 shows weight variation of the samples during the aging test. All samples showed an increase in weight, which indicates generation of degradation products during the aging test. Increase in the weight of AP/Mg was much greater than that of Mg(MgSt) and Mg(PD). It means that the degradation progress of AP/Mg(MgSt) and AP/Mg(PD) was lower than that of AP/Mg. The results show that MgSt and PD coatings worked as stabilizers against humidity. Meanwhile, a comparison of the results of AP/Mg(MgSt) and AP/Mg(PD) indicated that the stabilization effect of PD coating was higher than that of Mg(MgSt) coating.

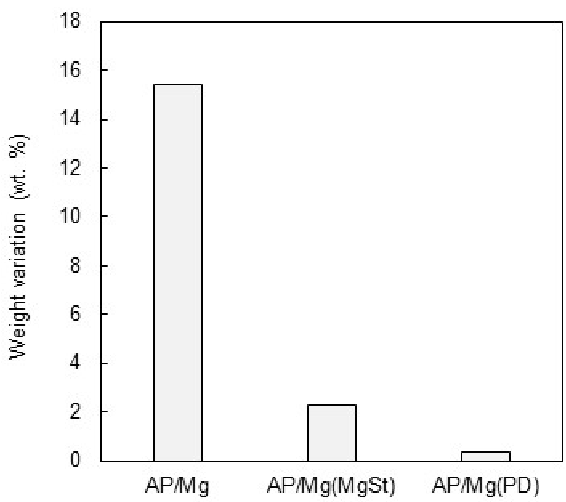

Figure 4. Weight variation of samples during aging test.

3.1 Burning test

The results of burning test and flame spectrum are exhibited in Table 2 and Figure 6, respectively. All samples could ignite easily.

Table 2. Burning t rate of samples.

No.	Sample name	Average burning rate [mm/s]	Standard deviation [-]
1	AP/HTPB/Mg(MgSt)	1.4	0.047
2	AP/HTPB/Mg(HSt)	1.3	0.0
3	AP/HTPB/Mg(CaSt)	1.4	0.15
4	AP/HTPB/Mg/MgSt	1.4	0.047
5	AP/HTPB/Mg	1.8	0.077

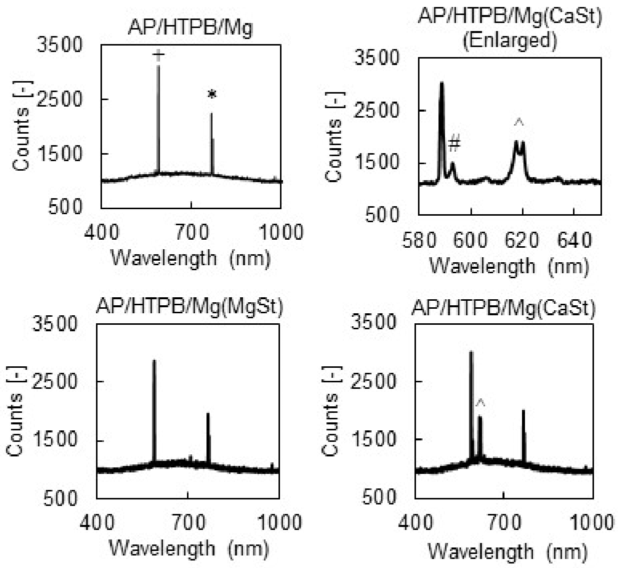

Figure 5. Spectrum of flames.
(+: 589 nm, #: 593 nm, ^: 613-622 nm, *: 767 nm)

The difference of the burning rate between AP/HTPB/Mg and AP/HTPB/Mg(MgSt) indicated that coating with MgSt decreased the burning rate of AP/HTPB/Mg. Data from Table 2 show that coating with HSt and CaSt can further decrease the burning rate. Although the contribution of weight from stabilizers was about 3%, the decrease in the burning rates was over 15%. Therefore, the weight change of the burning component was marginal before and after the addition of stabilizers. Thus, the chemical effect of the stabilizers could be considered to be the key element that decreased the burning rates. Comparison between AP/HTPB/Mg(HSt) (Sample 2) and AP/HTPB/Mg (Sample 5) revealed that the decrease in the burning rate originated from the stearate ion. The burning rate of AP/HTPB/Mg/MgSt, which was a simple mixture of AP, HTPB, Mg, and MgSt (Mg was not covered with MgSt), also decreased similar to Mg coated with MgSt. The effect of MgSt coating on the burning rate was lesser than the effect when MgSt existed within the sample. From these burning tests, it is clear that stearate posed a negative effect on the combustion rate.

Figure 5 shows the spectrum of flame, a characteristic property of fireworks. A slight difference was observed in the spectra of AP/HPTB/Mg and AP/HTPB/Mg(MgSt). The MgSt coating exhibited a slight effect on the color of flame in pyrotechnics. All samples showed peaks at 589 nm and 767 nm, which are attributed to sodium atomic emission and potassium atomic emission, respectively [17]. Previous experiments revealed that the observed emission originated in AP[17][18]. The spectrum of AP/HTPB/Mg(CaSt) shows peaks at 593 nm and 620 nm, which result from calcium monochloride [17].

4 Conclusion

In order to develop a better stabilizer than the existing ones, the effects of MgSt coating on the aging and combustion of pyrotechnic compositions containing Mg were investigated.

Aging test revealed the stabilization effect of MgSt coating. MgSt prevented the generation of $Mg(OH)_2$, the main degradation product of the reaction of AP/Mg with moisture. The results show that MgSt serves as a stabilizer against the aging of Mg in AP/Mg. However, MgSt coating showed less stabilization effect than the harmful traditional stabilizer, PD. There is room for further improvement of MgSt stabilizer for the development of pyrotechnic compositions.

Results of burning tests indicated that stearate coating (MgSt, HSt, or CaSt) on Mg decreased the burning rate. The decrease in the burning rate of samples with MgSt, either coated on Mg or present within, revealed that stearate induced a negative effect on the combustion rate. Burning test revealed that MgSt was less influential in affecting the flame color. This study shows that MgSt can be a suitable stabilizer for pyrotechnics to meet the requirements in terms of light emission and environment. This information on the effects of MgSt is expected to help in designing pyrotechnic compositions with MgSt as a stabilizer.

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