

IV. Conclusion

The problem of response of a rectangular plate subjected to a diagonal line-load which is, in addition, a function of time has been obtained in closed form by means of operational calculus. The results for the deflection and the moments are given in a simple form such that they can be used by any engineer working in the field without any practical difficulty. Two examples are presented to illustrate the theory. The rapid convergence of the solution has been indicated.

Effect of Lithium and Ammonium Fluorides on Ammonium Perchlorate Decomposition

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Introduction

THE importance of the thermal decomposition studies on ammonium perchlorate (AP) using metal oxides and fluorides as additives originates mainly from the fact that these additives are used to modify the burning rates of AP-based solid composite propellants. Recently, we reported the catalytic effect of some metal perchlorate amines on the thermal decomposition of AP.^{1,2} It was noticed that the metal oxides catalyze the AP decomposition by forming the metal perchlorate amines as intermediates. No thermal decomposition study on AP appears to have been made using the metal fluorides as additives, although lithium fluoride has been reported to be acting as a burning rate retardant when used as an additive to AP-based propellants.³⁻⁵ Similarly, ammonium and lithium fluorides appear to have a significant effect in inhibiting the burning rate of AP.⁶⁻¹⁰ It is therefore interesting to examine the effect of these fluorides on AP decomposition.

Experimental

Lithium fluoride and ammonium fluoride were available commercially (National Fluorine Corporation, India) and were used as such. Ammonium perchlorate (Fluka AG, 99.5% purity) was used after recrystallization. Differential thermal analysis (DTA) and thermogravimetric (TG) analysis were carried out in air using platinum cups as sample holders. The heating rates employed were 12 deg/min and 5 deg/min in the case of DTA and TG, respectively. LiF:AP (1:10) and NH₄F:AP (1:10) mixtures (by weight) were prepared and used on the same day.

Results and Discussion

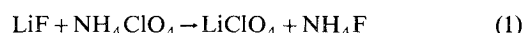
LiF:AP System

The DTA of pure AP shows an endotherm peaking at 240°C due to phase transformation and two exotherms at 300 and 390°C due to decomposition. Under identical conditions, the DTA curve of AP remains virtually unchanged when LiF is added to it in a 1:10 weight ratio. This shows apparently no chemical reaction between LiF and AP. However, the isothermal TG of the mixture show interesting behavior (Fig. 1). In the low temperature region, i.e., at 270°C, AP

decomposes to about 25% before reaching saturation, whereas in presence of LiF an apparent desensitization of decomposition is observed. At higher temperatures, although AP decomposition is suppressed initially upon addition of LiF, it decomposes rapidly after an induction period. This induction period decreases as the temperature increases. For example, the induction period at 295°C is 200 min, while at 348°C it is only 10 min. The analysis of the residue left behind at the end of the runs showed the presence of lithium perchlorate.

Isothermal TG of LiClO₄:AP (1:1) mixture at 295°C showed rapid decomposition of AP without any induction period. A behavior similar to 10% concentration of LiF was observed when lower concentrations, viz, 1, 2, and 5% were used.

This strange effect of LiF on AP decomposition—essentially inactive in dynamic heating conditions but exhibiting activity under isothermal conditions—is essentially due to the fact that longer time is needed for the reaction to occur between the fluoride and AP, which may take place as postulated earlier^{5,7,9}:



The lithium perchlorate thus formed appears to catalyze AP decomposition at higher temperatures. It is reported^{11,12} that the LiClO₄:AP system forms a eutectic mixture, melting at 182°C, which is known to catalyze the AP decomposition. The observed catalytic activity at 290°C and above may therefore be due to the eutectic formation. The formation of lithium perchlorate in the LiF:AP system was confirmed by heating a mixture of LiF:AP (1:1 mole ratio) at 295°C for 10 hr. The product (melt) was highly hygroscopic, soluble in water, and gave positive tests for Li⁺ and ClO₄⁻ ions. Further, as can be seen from Fig. 1, the isotherms showed a break at about 14% decomposition, before the onset of rapid decomposition. When the runs were interrupted at this point (14%), melt formation was observed in all cases.

In order to explain the apparent desensitization of AP up to 14% decomposition in presence of LiF, the effect of other, analogous additives, e.g., NaF, MgF₂, on AP decomposition was studied. The DTA of NaF:AP (1:10) and MgF₂:AP (1:10) mixtures under identical conditions did not show any catalysis, i.e., there was hardly any change in the ignition temperatures of AP. But isothermal TG curves (Fig. 2) of the mixtures at 270°C showed suppression in the decomposition of AP, similar to LiF. However, there was no catalysis of AP

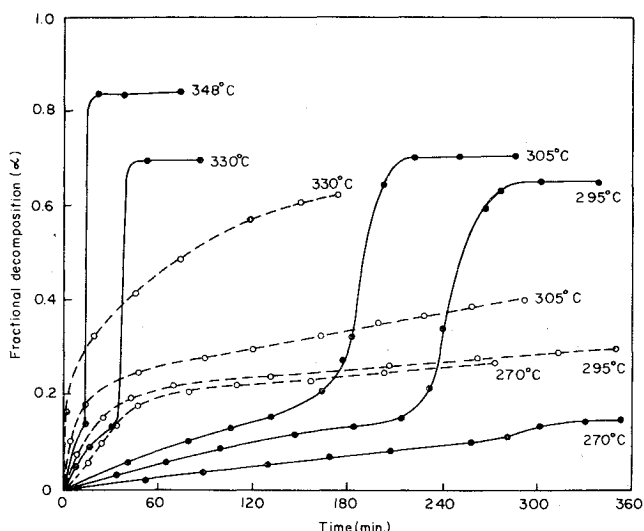


Fig. 1 Isothermal TG curves of LiF:AP (1:10) mixtures (—) and AP(---) at various temperatures.

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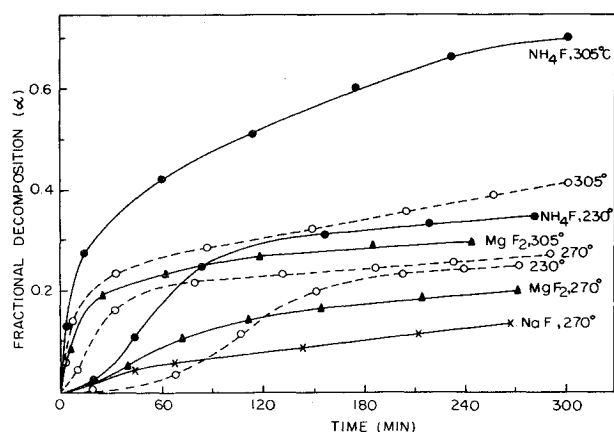


Fig. 2 Isothermal TG curves of NH_4F , NaF , and MgF_2 :AP (1:10) mixtures (—) and AP (---).

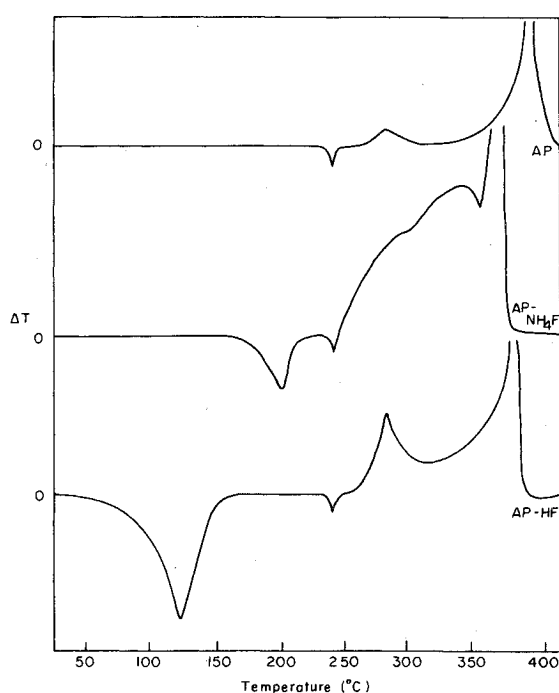


Fig. 3 DTA curves of NH_4F :AP (1:10), HF:AP mixtures, and AP in air.

decomposition at higher temperatures, as evidenced by MgF_2 :AP isotherm at 305°C.

The apparent desensitization in these cases may be explained by assuming a similar reaction in these cases, i.e.,



The formation of sodium perchlorate in the NaF :AP (1:1 mole ratio) system was confirmed by heating the mixture at around 300°C for 10 hr and analyzing the product, which gave negative test for F^- ions. The isothermal TG of the mixture at 305°C showed weight loss corresponding to NH_4F sublimation. The apparent desensitization of AP with the addition of these fluorides may therefore be due to the volatilization of NH_4F as it is being produced. No significant decomposition of AP, as such, appears to take place while the fluoride is being consumed and volatilized as NH_4F . The lack of catalytic activity at higher temperatures in the case of Na and Mg fluorides is probably due to the absence of melt (eutectic) formation in these cases. At this stage it was thought worth while to investigate the effect of ammonium fluoride on AP decomposition.

NH_4F :AP System

The dynamic TG of the NH_4F :AP (1:10) mixture shows initial weight loss corresponding to the amount of NH_4F present in the mixture. The overall decomposition of AP, however, occurs at lower temperatures in the presence of NH_4F . In DTA as shown in Fig. 3, two endotherms at 200 and 240°C are observed, corresponding to decomposition and sublimation of NH_4F and orthorhombic to cubic phase transformation of AP, respectively. The first exotherm of AP decomposition at 300°C shows an increase in the intensity of the peak, and the peak temperature of the second exotherm is lowered to 370°C from 390°C. Both TG and DTA therefore show overall sensitization in the decomposition of AP, although NH_4F volatilizes away at much lower temperatures.

The isothermal TG (Fig. 2) of the NH_4F (1:10) mixtures show that NH_4F catalyzes AP decomposition. In contrast, it should be noted that NH_4F inhibits AP self deflagration.^{6-8,10} It is well known that NH_4F ¹³ decomposes to $\text{NH}_3(\text{g})$ and $\text{HF}(\text{g})$ around 200°C. But $\text{NH}_3(\text{g})$ is reported¹⁴ to suppress AP decomposition. The observed catalytic activity of NH_4F may be due to $\text{HF}(\text{g})$ etching the surface of AP crystals while escaping, thereby producing the defects which seem to catalyze AP decomposition. A DTA experiment with a drop of $\text{HF}(\text{aq})$ added to AP showed sensitization of the first exotherm at 300°C of AP. Also, the final decomposition temperature of the second exotherm decreased (Fig. 3). The observed effect on AP decomposition of the addition of NH_4F appears to be somewhat different than that of metal fluorides. However, in the later cases NH_4F is produced in-situ, as a result of chemical reaction, and volatilizes on the surface itself as soon as it is produced, thus providing no opportunity for etching the surface.

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