

NOTE**Radiation Effects on Thermal Decomposition of Neutron Activated Ammonium Perchlorate**

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Isothermal decomposition of neutron activated ammonium perchlorate mixed with 3% by weight of NH_4MnO_4 was studied after giving 12 Mrad γ -radiation dose and heat treatment at 250 and 275°C. The rate and the extent of decomposition increased at both the temperatures. The rate constants for acceleratory and decay stages are calculated.

Ammonium perchlorate is widely used in solid composite propellants as an oxidizer. Its thermal stability depends on the presence of additives¹. Additives alter the decomposition characteristics of ammonium perchlorate because of the structures and chemical properties. Composite solid propellants^{2,3} were studied using different transition metal oxides. To understand the catalytic action on thermal decomposition of the oxidizer and burning characteristics of the propellant this work is undertaken.

Imperfection in structure influences the reactivity of solids. The treatment of the crystals specially at the decomposition temperature increases the number of dislocations in the vicinity of the nuclei. It was observed⁴ that the pre-irradiation by ^{60}Co γ -rays with 10 MGy dose accelerated the thermal decomposition of pure ammonium perchlorate. Therefore, it was of interest to understand the effect of γ -irradiation on the thermal decomposition characteristics of neutron activated ammonium perchlorate at different temperatures.

EXPERIMENTAL

Ammonium permanganate was prepared as discussed elsewhere by the method suggested by Bircumshaw and Taylor⁵. The NH_4MnO_4 crystals were recrystallised and powdered. Mixtures containing particles with about 70 microns size of 3% by weight of NH_4MnO_4 and crystallised commercial grade ammonium perchlorate were prepared. For neutron activation 252 Cf neutron source (Flux: $10^6 \text{ n cm}^{-2} \text{ s}^{-1}$) was employed. Neutron activation was effected for 2 h. Radiation treatment was carried out using 2 kCi ^{60}Co γ -source with rate 4.2 Krad/min. 100 mg of neutron activated and subsequently γ -irradiated sample was heated isothermally in a platinum cup and the loss in weight upon decomposition was

recorded. A single pan balance of 0.1 mg sensitivity and an electronically controlled furnace which maintained the desired temperature within $\pm 0-5^{\circ}\text{C}$ were employed for this study.

In the thermal decomposition the regions generally observed are puff region, induction region, acceleratory region, decay region and retention region. Out of these the acceleratory region, decay region and retention region are seen in decomposition of neutron activated ammonium perchlorate.

For pure ammonium perchlorate induction period is seen to be very small (Fig. 1). Rate over acceleratory region is moderate. The rate decreases slowly in

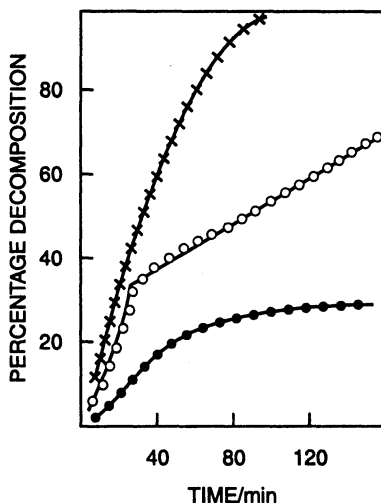


Fig. 1 Effect of γ -irradiation the thermal decomposition of ammonium perchlorate

- Pure ammonium perchlorate
- Ammonium perchlorate + 3% NH_4MnO_4 + 12Mrad γ -dose heated at 250°C
- × Ammonium perchlorate + 3% NH_4MnO_4 + 12Mrad γ -dose heated at 275°C

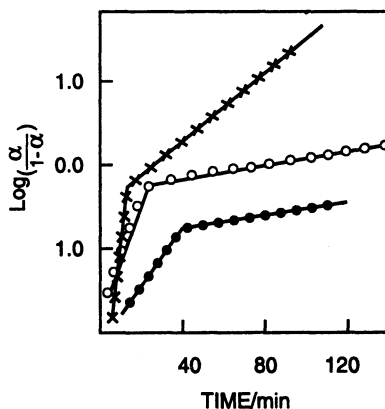


Fig. 2 Kinetics of thermal decomposition of ammonium perchlorate

- Pure ammonium perchlorate
- Ammonium perchlorate + 3% NH_4MnO_4 + 12Mrad γ -dose heated at 250°C
- × Ammonium perchlorate + 3% NH_4MnO_4 + 12Mrad γ -dose heated at 275°C

decay period. 35% total decomposition is observed. The mixture of 3% by weight of NH_4MnO_4 and the neutron activated ammonium perchlorate is irradiated upto 12 Mrad dose. When this mixture was heated at a temperature 250°C the retention of ammonium perchlorate decreased at 250°C from 70% to 20%. It becomes zero on heating the mixture at 275°C . Dedgaonkar *et al.* have reported⁴ complete decomposition of ammonium perchlorate at 225°C within 110 min only.

The data obtained was analysed using Prout-Tompkins equation⁶ $\log [\alpha/(1-\alpha)] = k_1 t + C$. Two straight lines resulted (Fig. 2) corresponding to each curve of Fig. 1. The rate constants obtained from the acceleratory (k_1) and decay (k_2) stages are presented in Table-1.

TABLE-1
RATE CONSTANTS k_1 AND k_2 (min^{-1}) FOR THE ACCELERATORY AND DECAY STAGES RESPECTIVELY IN AMMONIUM PERCHLORATE

	250°C		275°C	
	k_1	k_2	k_1	k_2
Pure ammonium perchlorate	0.032	0.005	—	—
Neutron activated ammonium perchlorate + 3% NH_4MnO_4 + 12 Mrad γ -dose	0.170	0.015	0.46	0.052

k_1 and k_2 at 250°C were observed to be much higher for neutron activated and gamma-treated mixtures than for pure ammonium perchlorate k_1 and k_2 are still increasing at higher temperature, *i.e.*, 275°C.

The temperature of decomposition of NH_4MnO_4 is much lower. At elevated temperature it disappears quickly and extensively damaged sites are created. Appreciable amounts of damage fragments like Cl^- , ClO_3^- , ClO^- etc. are produced⁷ upon exposure to γ -rays. It constitutes decomposition nuclei in the solid. The centres of decomposed material grow and it creates sufficient strain and hence breaking of crystal takes place. It creates new reactive surface and hence the reaction is faster in an acceleratory region.

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