

## Sensitizing Efficiency of Some Added Metal Salts on the Thermal and Explosive Characteristics of Hydrazenium Monoperchlorate and Hydrazenium Diperchlorate

C. PRABHAKARAN

Institute of Armament Technology, Pune-411025

N. SADASIVAN\*

Inspectorate of Military Explosives, Bhandara-441906

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**Abstract.** Sensitivity to heat, impact and friction of hydrazenium-monoperchlorate and hydrazenium-diperchlorate have been investigated and the sensitizing efficiency of some added metal salts evaluated. The thermal sensitizing efficiency of the additives follow the order  $CuCrO_4 > CuCl_2 > NiO > Fe_2O_3 > MgO$ . The activation energy values obtained from explosion delay time are comparable with the values reported for thermal decomposition studies and are close to the activation energy value for thermal decomposition of anhydrous perchloric acid. The F of I values for these compounds are in the range reported for common initiatory explosives and are of the same order as that for mercury fulminate.

### 1. Introduction

Hydrazenium perchlorates have been receiving increasing attention as a potential high energy oxidizer in solid propellant compositions. Although studies on the thermal decomposition characteristics have been carried out in recent years<sup>1</sup>, very little data is available in literature regarding their explosive properties. This study was, therefore, undertaken to evaluate the sensitivity of hydrazenium perchlorates to heat, impact and friction. The effect of particle size as well as sensitizing efficiency of various metal salts have been evaluated. It would be expected that the results will give useful information regarding stability, safety and storability of the compounds which are prerequisites to their possible use in explosive and propellant compositions.

### 2. Experimental

#### (a) Preparation of Compounds

*Hydrazenium-monoperchlorate*,  $N_2H_5ClO_4$ . The compound was prepared according to the method described by Levy *et al*<sup>2</sup>. The fine white crystals of the hemihydrate

\*Present address: NCML, Naval Dockyard, Bombay-400023.

salt,  $N_2H_5ClO_4 \cdot \frac{1}{2}H_2O$  were filtered in the cold through a sintered glass funnel and dried in a drying tube at 65–70°C for two hours under vacuum (0.05 mm Hg) to break down the hemihydrate. The hydrazine-monoperchlorate,  $N_2H_5ClO_4$  thus obtained had a melting point 138°C (literature value 137–138°C)

*Hydrazenium-diperchlorate,  $N_2H_6(ClO_4)_2$ .* The dihydrate salt  $N_2H_6(ClO_4)_2 \cdot 2H_2O$  was prepared by the method reported by Turrontine *et al*<sup>3</sup>. The precipitate was washed several times with cold 2-propanol and dried at 70°C for two hours under constant vacuum (0.05 mm Hg) to obtain the  $N_2H_5(ClO_4)_2$ . The crude product was dissolved in absolute ethanol at 60°C and reprecipitated with petroleum ether to obtain the pure compound. (Melting point 142°C; Literature value 142–143°C).

The purity of the salts as determined by titration<sup>3</sup> with 0.1 N NaOH was 99.86 to 99.9 per cent.

### (b) Sensitivity Studies

*Thermal Sensitivity measurement.* A woods metal bath similar in design to the one used by Copp *et al*<sup>4</sup> was employed for measuring the explosion delay time. The bath was equipped with a dimmerstat to facilitate temperature control. A thermometer immersed in the molten woods metal bath recorded the temperature to an accuracy of  $\pm 0.1^\circ C$ . About 20 mg of the samples were enclosed in an aluminium cap, 5 mm dia and 5 mm depth, and dropped into the metal bath maintained at pre-determined temperatures. The interval between the time of insertion of the capsule and the moment of explosion or puffing was noted by a stop watch for recording the explosion delay time at the given temperature. A minimum of five readings were taken at each temperature and the average taken.

*Impact Sensitivity by Drop-Weight Method.* An apparatus similar in design to the one used by Taylor and Weale<sup>5</sup> was used for measuring the impact sensitivity. About 2 mg sample was taken for each experiment and a steel ball of 2.2 cm diameter weighing 28.35 gm was used as the dropping weight. Ten readings were taken at each height and the percentage of explosion noted. The height required for 50 per cent explosion was obtained graphically.

*Friction Sensitivity Test.* Friction sensitivity was measured both by Mallet<sup>6</sup> friction test and Torpedo<sup>7</sup> friction test. In Torpedo test about 10 mg sample was spread on the mild steel anvil and struck with one kg weight torpedo having a mild steel head. Ten trials were carried out in each case and the percentage of explosion noted.

## 3. Results and Discussion

### (a) Thermal Sensitivity

The explosion delay times for hydrazenium-monoperchlorate (HP) and hydrazenium-diperchlorate (HP-2) were measured, on three different particle sizes, in the temperature range 200–280°C after every 10°C rise in temperature. The delay times at 270°C are given in Table 1. Thermal sensitivity increases with decrease in particle size. HP is comparatively more sensitive thermally than HP-2. The activation energy

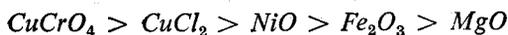
**Table 1.** Induction period at 270°C temperature of explosion and energy of activation values.

Sieve size (Taylor Standard)	Explosion delay at 270°C (Sec)	Temp of explosion for 5 seconds delay (°C)	E Values (k cal mole <sup>-1</sup> )
HP Coarse	6.1	285	23.5
100	5.4	275	22.4
200	4.9	268	20.6
HP-2 Coarse	6.8	288	24.3
100	5.8	280	23.0
200	5.3	274	21.8

values were obtained from explosion delay time using the relationship<sup>8,9</sup>:  $\log \tau = \frac{E}{4.75 T} + B$  and are included in Table 1. These values are comparable to the activation energy values reported for thermal decomposition studies of these compounds<sup>10,11</sup>. Gralecki and Cruice<sup>10</sup> have reported 23.8 k cal mole<sup>-1</sup> for HP in the temperature range 140–200°C and 23.5 k cal mole<sup>-1</sup> for HP-2 in the temperature range 100–150°C. The activation energy reported for decomposition of anhydrous perchloric acid<sup>12</sup> is 22.2 k cal mole<sup>-1</sup>. This close similarity in the activation energy values would indicate that the physico-chemical processes controlling the decomposition in all these cases are more or less of a similar mechanism.

The temperatures of explosion (for five seconds delay) as estimated from the plot of explosion delay time versus temperature are 268°C and 274°C respectively for HP and HP-2.

*Effect of Additives on Thermal Sensitivity.* Dry finely ground metal salts such as  $\text{CuCrO}_4$ ,  $\text{CuCl}_2$ ,  $\text{NiO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$  were intimately mixed with 200 mesh size HP and HP-2 and the explosion delay times measured. These additives were found to sensitize HP and HP-2 by varying degrees. In order to find the optimum level of additive needed to give maximum sensitizing effect, the explosion delay measurements were carried out by varying the concentration of additives in the mixture from 1 to 5 per cent by weight. The activation energy values estimated in each case are plotted against their percentage weight in Fig. 1. It can be seen that in all cases there is an optimum level which gives maximum sensitizing effect and any addition beyond this amount has a marked desensitizing action. For example maximum sensitizing of HP-2 is observed with four percent by weight of  $\text{CuCrO}_4$  when the temperature of explosion decreases from 278°C (for pure HP-2) to 240°C and the activation energy value decreases from 21.8 k cal mole<sup>-1</sup> (for pure HP-2) to 11.8 k cal mole<sup>-1</sup>. Similar trend in decrease of activation energy and ignition temperature has been reported in the decomposition of ammonium perchlorate catalysed by chromic oxide<sup>13</sup>. Based on activation energy values, both for HP and HP-2 (Table 2) the following order of sensitizing efficiency has been observed:



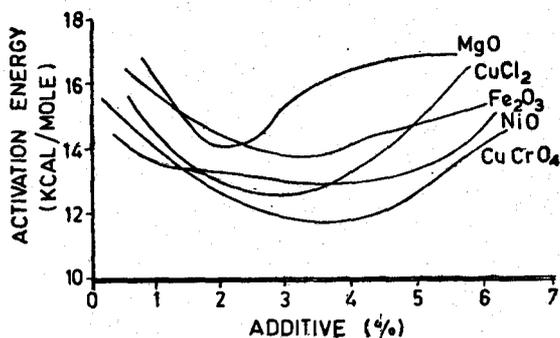


Figure 1. Effect of additives on activation energy of HP-2.

Table 2. Temperature of Explosion and Activation Energy Values for HP-2 in Presence of Optimum Per cent of Additives.

Additive	Optimum weight (%)	Temp. of explosion (°C)	<i>E</i> Values (k cal. mole <sup>-1</sup> )
Cupric Chromate	4	240	11.8
Cupric Chloride	4	245	12.4
Ferric Oxide	3	250	13.4
Nickel Oxide	2	250	12.5
Magnesium Oxide	2	255	18.6

Levy and Coworkers<sup>2</sup> have found that the deflagration of hydrazenium perchlorate gets catalysed and proceeds reproducible when small concentration of metal salts are added. Since the catalysed reaction exceeds the rate of uncatalysed one. It is felt that the  $HClO_4$  produced migrates to the catalyst surface by diffusion and then decomposes heterogeneously. Same mechanism might be operative in thermal sensitivity studies in which the  $N_2H_4$  and  $HClO_4$  molecules formed diffuse to the catalyst surface and their subsequent exothermic reaction result in accelerated decomposition leading to explosion. In presence of the additives studied the activation energy values generally lie between 11 and 16 k cal mole<sup>-1</sup>. At optimum concentration of the catalyst the heat content of the surface probably increases and catalyses the exothermic reaction. At higher concentration of additives, the catalysing effect of the exothermic reaction would outweigh the heat loss effect which accounts for the decrease in sensitizing effect.

#### (b) Impact Sensitivity

The impact sensitivity of HP and HP-2 were measured on gently ground samples sieved through 75, 100, 150 and 200 mesh (Taylor) sieves. The median heights (for 50 per cent explosion) obtained for each of the fractions retained on the respective sieves are shown in Table 3. HP-2 is slightly more sensitive than HP. Sensitivity progressively decreases with the decrease in particle size. This trend is just the reverse of what was observed for thermal sensitivity.

Various investigators<sup>15,16</sup> have shown that initiation of explosion by impact is thermal in origin and is dependent on crystal size and also on concentration of defects within the crystal lattice. Impact creates hot spots in the explosive, the temperature of which may be high enough for the decomposition to take place at such a rate that the reaction must remain essentially adiabatic once the hot spot is created. The reaction therefore, continues to accelerate until explosion occurs. If the crystals are too small the reaction will not grow to explosion unless the energy injected is high enough to activate a proportion of the molecule so that they explode thermally. The impact sensitivity data of HP and HP-2 are compared with some common initiatory explosives in Table 4. The F of I values for HP and HP-2 are comparable to these initiator compounds and are of the same order as that for mercury fulminate.

**Table 3.** Median Drop Heights for HP and HP-2 with Variation in Particle Size

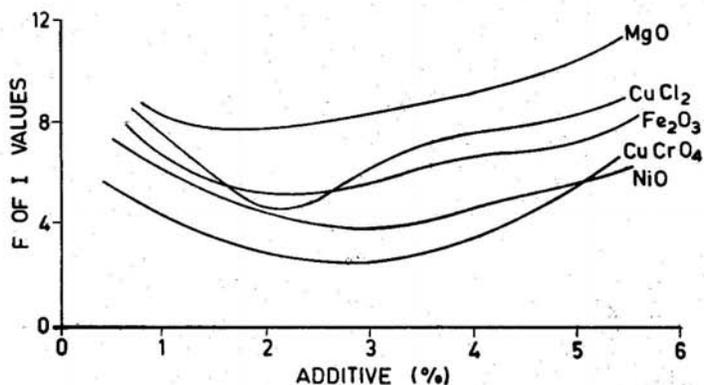
Weight of ball = 28.35 gm; diameter of ball = 2.2 cm

Sieve size (Taylor Standard)	Median drop height in cm	
	HP	HP-2
Unground	40.0	30.0
75	38.0	28.0
100	40.5	28.5
150	43.0	30.5
200	48.5	35.5

**Table 4.** F of I Values of HP and HP-2 and Initiatory Explosives

Explosive	Height for 50% Explosion (cm)	F of I Values	Ref
HP	38.0	13.5	This work
HP-2	28.0	9.9	-do-
Mercury Fulminates	28.1	10.0	6
Lead Azide	45.5	19.2	17
Lead Styphnate	45.5	21.5	17

Impact sensitivity of HP-2 in presence of the additives ranging from 1 to 5 per cent by weight were measured. The F of I values calculated using mercury fulminate standard show that impact sensitivity is significantly enhanced in the presence of these additives. As with thermal sensitivity the impact sensitivity also reaches maximum at an optimum concentration of the additive above which the sensitizing efficiency



**Figure 2.** Variation of impact sensitivity of HP-2 with level of additive.

decreases. The effect of additives on the F of I values is illustrated in Fig. 2. The sensitizing efficiency of the additives follow the order :



The order of impact sensitizing efficiency of the additives do not follow the same order as for thermal sensitizing efficiency, but appears roughly related to the hardness of the additive. Bowden and Gourton<sup>15</sup> have shown that in impact sensitization the function of catalyst additives is to act as grit particles. Thus if grit effect is the main criterion for increasing impact sensitivity it would be expected that a number of inert and hard additives would act as sensitizers.

### (c) Friction Sensitivity

HP is more sensitive to friction than HP-2 but both are comparatively less sensitive to friction than mercury fulminate and lead azide. In case of HP-2, 50 per cent explosions occurred (out of 10 trials) with stone anvil and no explosion with a hard wood anvil, whereas in HP 60 per cent and 30 per cent explosion occurred respectively with stone anvil and hard wood anvil. Similar trend is exhibited in the torpedo friction test.

The friction sensitivities are appreciably increased in presence of the additives and the sensitizing efficiency follows the same order as impact sensitivity. However, no well defined optimum level of additives could be observed in the 1 to 5 per cent range studied, although an increase in sensitivity is apparent with additives in the 4 to 5 per cent range. Similar to impact explosion, initiation of explosive by friction is also ascribed to formation of hot spots. Thus grit effect and melting point of the additives would be expected to be the controlling factors.

## 4. Conclusion

HP is more sensitive to heat and friction than HP-2. Sensitivity to impact is higher for HP-2 than HP. The temperature of explosion, the activation energy values as well as F of I values for both compounds are in the range reported for common initiatory explosives. The friction sensitivity of both HP and HP-2 are comparatively less than that of the initiatory explosives. The sensitivity to heat, impact and friction are significantly enhanced in presence of such additives as  $CuCrO_4$ ,  $CuCl_2$ ,  $Fe_2O_3$ ,  $NiO$  and  $MgO$ . The sensitizing efficiency reaches a maximum at an optimum level of additive beyond which the sensitivity rapidly decreases.

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## References

1. Levy, J. B., Von Elbe, R., Friedman, Wallin, T. & Adams, S. J., 'Advances in Propellant Chemistry' (American Chemical Society Publication), 1965.
2. Levy, J. B., Friedman, G. & Adams, S. J., 'Advances in Propellant Chemistry' (American Chemical Society Publication), 1965.
3. Turrontine, J. W. & Gill, A. C., *J. American Chemical Society*, **37** (1915), 1122.
4. Copp, J. L. & Napier, S. F., *Phil. Roy. Society (London)*, **197** (1949), 241.
5. Taylor, W. & Weale, A., *Proc. Roy. Society*, **138A** (1932), 92.
6. 'Service Text Book of Explosives' JSP-393 (1972) Chap. 14.
7. Fordham, S., 'High Explosives & Propellants' (Pergamon Press Ltd., Oxford, London) 1966, p. 75.
8. Singh, K., *Trans. Faraday Society.*, **124**, (1959) 55.
9. Cook, M. A., 'The Science of High Explosives' (Reinhold Publishing Corp., N. Y.), 1958, p. 174.
10. Gralecki, C. J. & Cruice, W., 'Advanced Propellant Chemistry' (Advances in Chemistry Series, American Chemical Society Publication), 1965, p. 73.
11. Sadasivan, N. & Navale, N. G., *J. Armament Studies*, **11** (1975), 23.
12. Sarner, S. F., 'Propellant Chemistry' (Reinhold Publishing Corporation, N. Y.), 1966, p. 296.
13. Hermoni, A. & Salmon, A., '8th International Symposium in Combustion', (Williams and Wilkins Co., Baltimore) 1962, p. 656.
14. Jacobs, P. W. M. & Russal Jones, A., *Can. J. Chemistry*, **44** (1966), 2435.
15. Bowden F. P. & OAJ. Gourton, *Proc. Roy. Society, (Lond)*, **A198**, (1949), 350.
16. Garner, W. E., *Trans. Faraday Society*, **34** (1938), 985.
17. 'Military Explosives' (Deptt of Army & Air Force, Technical Manual, Washington) Sec V, 1955.