Defence Science Journal, Vol 48, No 3, July 1998, pp. 303-308


# Effect of Tammann Temperature and Relative Humidity on Lead Chromate and Magnesium-Based Compositions

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**ABSTRACT**

Smoke and flash composition based on $PbCrO_4$ and $Mg$ powder in the ratio 80:20 is a binary composition intended to produce orange smoke and brilliant white light on ignition. $PbCrO_4$ acts both as an oxidiser and the colouring agent.The composition is highly sensitive to shock and friction as its friction and impact sensitivities are 36 and 195, respectively. Inspite of its inert nature, the composition self-ignited on two ocassions, during mixing and processing, resulting in disastrous fires and widespread damage to life and property. The ignition of high energy mixture occurs when the reactants acquire activation energy to be in a reactive state. In this state, the reaction occurs with the release of considerable energy. This paper deals with the effect of Tammann temperatue *vis-a-vis* the moisture content of the composition in inducing self-ignition in the energetic mixture.

## NOMENCLATURE

| | |
|---|---|
| $\Delta G$ | Change in free energy |
| $\Delta G^\circ$ | Change in free energy at standard state |
| $T$ | Temperature |
| $P$ | Pressure |
| $\Delta H$ | Change in heat of reaction. |
| $\Delta S^\circ$ | Change in entropy at standard state |
| $K$ | Degree Kelvin |
| $MW$ | Molecular weight |
| $n$ | Moles |
| $\Sigma$ | Summation |
| $S$ | Solid |
| $V$ | Vapour |
| $T_o$ | Ignition temperature |
| $T_{max}$ | Maximum temperature of ignition. |
| $\alpha$ | Ratio of temperature of solid/T melting point in degree Kelvin. |

## 1. INTRODUCTION

One of the primary concerns in handling pryotechnic mixtures is their accidental ignition. An indigenously developed smoke and flash composition based on $PbCrO_4$ and $Mg$ powder in the ratio 80:20 has shown two such mysterious explosions during processing and mixing. The objective of this study was to make a thermodynamic determination of spontaneity of chemical reaction between $PbCrO_4$ and $Mg$ powder.

## 2. SPONTANEITY OF REACTION MIXTURES

The ignition of high energy mixtures occurs when the reactants acquire activation energy to be in a reactive state. Rate of a chemical reaction is determined by this activation energy which is the threshold energy barrier that must be crossed. It also depends on temperature. As the temperature of a system is raised, an exponentially greater number of molecules acquire the necessary activation energy causing an exponential increase in reaction rate. A thermodynamic condition in an

Received 01 April 1997, revised 23 September 1997

energetically vibrant system that leads to rise in temperature can therefore set off self-ignition. Whether a reaction is spontaneous or will actually take place only when the fuel and the oxidiser are mixed together, is determined by a quantity known as free energy ($G$)[1]. The criteria of spontaniety is:

$\Delta G < 0$ (irreversible process)

To decide whether a certain change of state is spontaneous, the accompanying free energy change need to be evaluated at standard condition by the equation:

$$\Delta G^{\circ} = \Sigma G^{\circ} \text{ (products) ------ } \Sigma G^{\circ} \text{ (reactants)}$$

A large negative value of $G$ indicates an exothermic and spontaneous chemical reaction.

## 3. THERMOCHEMISTRY OF THE SYSTEM

The reaction between $PbCrO_4$ and $Mg$ in the ratio (80:20) satisfies this criterion of spontaneity. The reaction is exothermic. The theoretically calculated value of $\Delta H$ for the exothermic reaction is -0.541 K cal/g and the experimentally calculated value is -0.640 to -0.686 K cal/g. $T_o$ is 585 °C and $T_{max}$ is 603 °C calculated using differential thermal analyser (DTA). Because of the high values of $T_o$ and $T_{max}$, there is an increase in the entropy of the system. All chemical reactions that involve an increase in entropy will occur spontaneously if the temperature is high enough. As the temperature of the system is raised, an exponentially greater number of molecules will possess the necessary energy of activation. In this excited state, the reaction will occur releasing considerable energy. A sudden rise in temperature in a high energy mix can therefore set off a reaction. The composition under study has self-ignited on two ocassions.

The possible cause for sudden temperature rise in the mixture is due to the exothermic reaction between $Mg$ and moisture present in the composition. The Tammann temperature of $PbCrO_4$ is 311 °C (based on DTA). The combination of low Tammann temperature of $PbCrO_4$ and exothermic reaction of $Mg$ with $H_2O$ accounts for the mysterious explosion of the composition under study. The effect of Tammann temperature and moisture on the chemical kinetics of reaction, leading to energetically favourable condition of spontaneity is investigated.

## 4. THERMODYNAMIC & THERMOCHEMICAL EVALUATION

The chemical reaction of the mixture can be represented by the following probable exothermic reaction:

$$6PbCrO_4 + 9Mg \rightarrow 6PbO + 9MgO + 3Cr_2O_3 + \Delta H - 0.516 \text{ K cal/g} \quad (1)$$

$$6PbO + O_2 \rightarrow 2Pb_3O_4 + \Delta H \text{ -0.025 K cal/g} \quad (2)$$

$$\text{Net } 6PbCrO_4 + 9Mg + O_2 \rightarrow 2Pb_3O_4 + 9MgO + 3Cr_2O_3 + \Delta H - 0.541 \text{ K cal/g}$$

The experimentally calculated heat of reaction at the Controllerate of Military Explosives, Kirkee, is 640 to 680 K cal/g. The reaction though exothermic has a moderate heat output. The number of moles of $Mg$ that can be vaporised by this energy for the following reaction:

$$6PbCrO_4 + 9Mg \rightarrow 6PbO + 9MgO + 3Cr_2O_3 \quad (3)$$

is theoretically calculated as:

$$n = \frac{\Delta H^{\circ} 298}{\Delta H^{\circ}[Mg \text{ 1390 K} - Mg^{s} \text{ 298 °K}]} = \frac{1113.53}{30.75} = 36.2$$

$\Delta H^{\circ}$ 298 for the reaction (3) = 1113.53 K cal

$\Delta H^{\circ}$ for $Mg$ (vapour) at vaporisation temperature (1390 K) = 30.75

$\Delta H^{\circ}$ for $Mg$ (solid) = 0

The weight percentage of $Mg$ for the optimum composition from Eqn (3) is

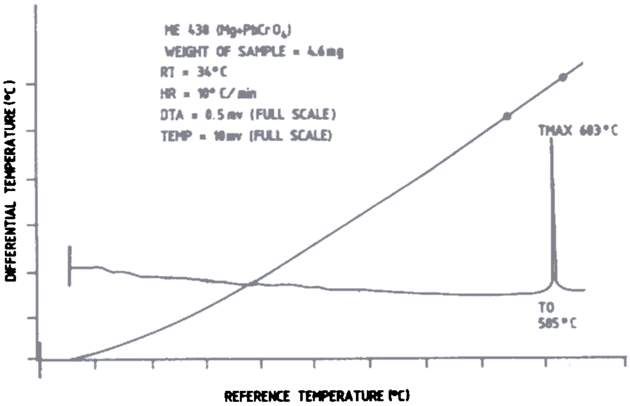


**Figure 1. Thermogram of $PbCrO_4$ + $Mg$ mixture**

$$\frac{(9+n)\ (\text{MW } Mg)\ 100}{(9+n)\ (\text{MW } Mg) + 6\text{MW } PbCrO}$$

$$\frac{1099.54}{3038.74} = 36.18 \text{ per cent}$$

The heat output of the reaction can therefore vaporise maximum of 36.18 per cent of $Mg$ in the mixture, whereas the mixture contains only 20 per cent of $Mg$. It shows that the fuel has been completely consumed and a sustained and complete burning has taken place.

## 5. COMPUTATION OF STANDARD FREE ENERGY CHANGE OF THE REACTION

$$\Delta G^o = \Sigma G^o f(\text{products}) - \Sigma G^o f(\text{reactants})$$
$$= 2(-45.25) + 9(-135.31) + 3(-250.30)$$
$$-6(203.60) + 9(0)$$
$$= 2059.19 + 1221.6 = -837.59 \text{ K cal.}$$

**Table 1. Thermodynamic properties of lead chromate-magnesium reaction**

| Reactants | Molecular weight | Hf (K cal/mole) | Free energy (K cal/mole) |
|---|---|---|---|
| $PbCrO_4$ (s) | 323.2 | - 217.7 | - 203.60 |
| $Mg$ (s) | 24.312 | 0 | 0 |
| *Products* | | | |
| $Pb_2O_3$ (s) | 223.21 | - 51.5 | 45.25 |
| $MgO$ (s) | 40.32 | - 143.8 | 135.31 |
| Chromic oxide (s) | 152.02 | - 272.4 | 250.30 |

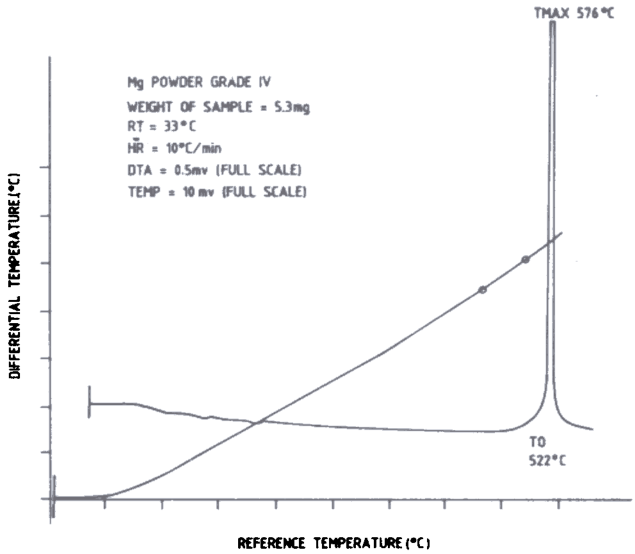


**Figure 2. Thermogram for the ingredient magnesium**

The criteria of spontaneity at condition $T,V$ constant is $\Delta G < 0$. In this state, the reactants in their standard states will be converted spontaneously to products in their standard states.

The above thermodynamic calculations indicate that $PbCrO_4$-$Mg$ reaction has the potential to attain spontaneity in view of large negative value of $G$ (Table 1).

## 6. TAMMANN TEMPERATURE AND ITS EFFECTS ON THE SYSTEM

DTA, carried out on the composition at the High Energy Materials Research Laboratory, Pune, indicates that the composition is igniting at 585 °C below the melting point and 319 °C below the decomposition temperature of $PbCrO_4$. The thermogram of $PbCrO_4$ /$Mg$ (Fig. 1) shows a violent exotherm near 585 °C. No crystalline transition is noticed. The thermogram for $Mg$ (Fig. 2) shows a violent exotherm near 522 °C without crystalline transition before $T_o$ is achieved. The $Mg$ is igniting

**Table 2. Physical properties of magnesium and lead chromate**

| Reactants | Melting point (°C) | Boiling point (°C) | Decomposition temperature(°C) |
|---|---|---|---|
| $Mg$ | 649 | 107 | |
| $PbCrO_4$ | 844 | | 904 |

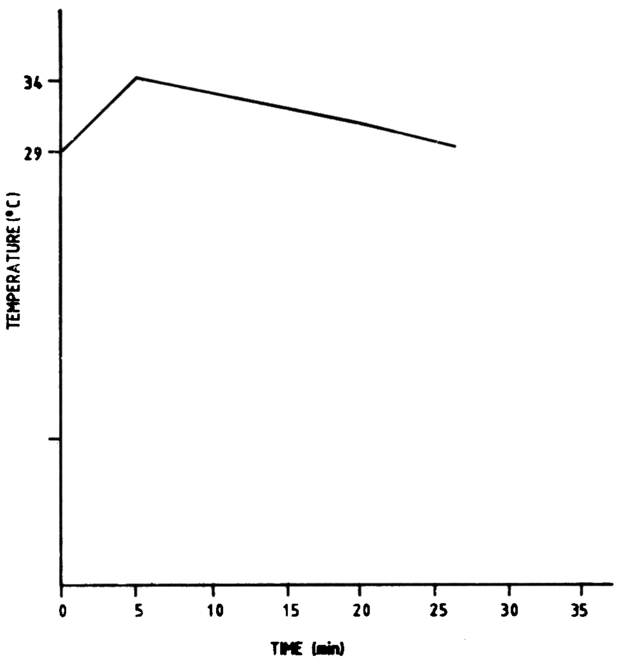


**Figure 3. Reaction of magnesium with 20 % water**

much below its melting point (Table 2). The ignition of the composition, much below the melting point of the oxidiser, is attributed to Tammann temperature. A rapid interaction between oxidiser and fuel in a pyrotechnic mixture can begin only when at least one of them is in liquid or vapour state. The oxidisers used in pyrotechnic mixtures are generally ionic crystals. The looseness of crystal lattices determines reactivity. The amplitude of vibrational motion of crystalline lattices increases as the temperature rises, and at melting point, a randomly oriented liquid state results due to collapse of forces holding the crystalline lattice together. If the vibrational amplitude of lattice of the solid oxidiser is sufficient, a liquid fuel can diffuse into it and can cause a reaction to occur. The lattice motion of the crystals can therefore greatly influence the reactivity.

According to Prof Tammann, if the actual temperature of the solid is divided by the melting point of the solid in Kelvin scale or absolute scale as per the following ratio[2]:

$$\alpha = \frac{T(\text{solid})}{T(\text{melting point in °K})}$$

the diffusion of mobile phase into crystalline lattice will be appreciable at an $\alpha$ value of 0.5 or half way to melting point on Kelvin scale. At this temperature termed as Tammann temperature, a solid has 70 per cent of its viabrational freedom and its diffusion into lattice becomes possible. Due to this, a chemical reaction between a good oxidiser and a mobile reactive fuel becomes possible. Tammann has shown that as a general rule, the diffusion of a mobile species into a crystalline lattice becomes appreciable close to 0.5 x melting point of solid in °K. When the solid-solid reaction occurs, the reactivity of a particular solid often shows a marked increase to the Tammann temperature of the reactants. The Tammann temperature of $PbCrO_4$ calculated using the DTA thermogram of the mixture is given below.

$$\text{Tammann temperature of } PbCrO_4 = \frac{585\ °\text{C}}{1117\ °\text{K}}$$
$$= 0.523$$

The Tammann temperature of $PbCrO_4$ is therefore 584.19 °K or 311 °C. A potential for chemical reaction between $PbCrO_4$ and $Mg$ therefore exists at 311 °C, if the diffusion of fuel into cryatalline lattice of $PbCrO_4$ becomes possible (Table 3).

**Table 3. X-ray crystallographic data of lead chromate[4]**

| System | Space group | a, b, c | Axial angle β |
|---|---|---|---|
| Monoclinic | C | 6.82, 7.48,7.16 | β= 102 deg .3 mts. |

If there is excess moisture in the system due to relative humidity (RH) of the processing room exceeding critical humidity 55 ± 5 per cent for the mixture, the temperature of the system increases due to the exothermic reaction of $Mg$ with $H_2O$, which is associated with the evolution of large amount of heat and gas.

### 6.1 Treatment of Magnesium With Water

The reaction of $Mg$ with $H_2O$ is exothermic. The change in temperature as a function of time when $Mg$ was treated with 20 per cent of water was studied at Quality Assurance Establishment (Military Explosives), Dehu Road.

$$H_2O + Mg \rightarrow MgO + H_2 + 78 \text{ K cal}^3$$

This is equivalent to 1.84 K cal/g of mixture [78/18 + 24.312]. The volume of gas liberated by the reaction is 530 cm$^3$. Figure 3 shows a graph indicating the change in temparature as a function of time when 1 g of $Mg$ was treated with 20 per cent $H_2O$. The hygroscopicity of the composition increases with the fineness to which its components are divided. The rate at which moisture is absorbed in the energetic mixture depends upon particle size of the constituents, its purity and the RH of the processing room. In the composition under study, the particle size of $PbCrO_4$ was < 0.5 μ, making the mixture highly susceptible to moisture absorption. The $PbCrO_4$ - $Mg$ system is potentially dynamic and can attain spontaneous ignition, as $Mg$ is capable of reacting with easily reducable $Pb$ ions present in the oxidiser in the electron transfer reaction

$$Pb^{+2} + Mg \rightarrow Pb + Mg^{+2}$$

The solubility product of $PbCrO_4$ is 1.8 x.10$^{14}$. The standard electrode potential of $Mg$ is -2.37 V and that of $Pb^{+2}$ is -0.126 V.

## 7. EXPERIMENTAL EVALUATION OF MIXTURE

### 7.1 Preparation of the Composition

The pyrotechnical binary was prepared first by coating $Mg$ powder (Gr. 4) with boiled linseed oil in a planetary mixer. After 72 hr of maturation, the coated $Mg$ was mixed with $PbCrO_4$ in the required ratio in a mixer under remote control. The RH of the mixing/processing room was maintained within 55 ± 5 %. The particle size of $PbCrO_4$ was maintained at 0.5 μ and purity 92 per cent. The purity of $Mg$ (Gr. 4) used was 98 per cent and apparent density 0.4 to 0.6 g/ml. The composition was then analysed to determine the percentage of ingredients and moisture content. The percentage composition of the ingredients was within the specification limits. The moisture content was between 0.26 to 0.30 per cent (permissible limit < 0.5 per cent).

### 7.2 Measurement of Heat of Reaction

The călorimetric value of mixture evaluated in Bomb calorimeter at Controllerate of Military Explosives, Pune, was between 640 and 680 cal/g. The dispersion was due to segregation/heterogeneous nature of the composition.

## 8. IGNITION PATTERN OF THE MIXTURE

$T_o$ and $T_{max}$ of the $PbCrO_4$ - $Mg$ composition were determined using DTA at HEMRL.

## 9. CONCLUSION

The ignition of smoke and flash composition based on $PbCrO_4$ and $Mg$ powder below the melting point of the oxidiser is possible, as conceived by Prof Tammann. If the system is moist, a compounding of heat evolution is obtained due to the heat released by $Mg$ and $PbCrO_4$ reaction. This is because of the exothermic decomposition of $PbCrO_4$ and the reaction between $Mg$ and the moisture absorbed in the system. The combination of low Tammann temperature of $PbCrO_4$ and the compounding heat evolution accounts for its unpredictable and mysterious ignition. Cartridges filled with smoke and flash composition under study, processed at RH > 55.5 per cent exhibited the following defects during storage:

(a) Bulging of cartridge cases made of $Al$ alloy having sheet thickness 0.75 mm, tensile strength 15.00 Kgf/mm$^2$, elongation 5.77 per cent and purity 99.6 per cent.

(b) Force-opening of the lid of cartridge cases at places where thickness of indentation was < 0.25 mm. During ISAT(B) trials, cartridge cases filled during high RH of the processing room have shown bulging of cartridge cases after four weeks of exposure. The procedure followed here can be extended to other pyrotechnical mixtures also to evaluate their safety.

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**Contributor**

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