

Reactivity of The Ternary Pyrotechnic System Red Lead – Silicon – Ferric Oxide

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ABSTRACT

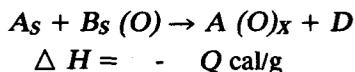
The reactivity of the ternary system of red lead, silicon and ferric oxide has been studied in comparison with the binary system red lead – silicon. Results from Differential Scanning Calorimetry (DSC) in nitrogen environment and Differential Thermal Analysis (DTA) in air have been supplemented with hot stage microscopy and combustion rate studies at about 30 atmospheres pressure. The ternary mixtures show three characteristic exotherms whose relative exothermicities vary with composition. DTA showed an unusual feature of a strong single exotherm at a certain critical mass which also varies with the composition. The critical mass could be reproduced within ± 1.0 mg. Hot stage microscopy of the pyrotechnic samples revealed strong surface mobility during the reaction leading to the formation of a sintered product. Self sustained combustion rates of the samples show an inhibiting effect by ferric oxide.

1. INTRODUCTION

Pyrotechnics cover a vast arena of applications in military and civil devices which have been used for centuries little realizing the fundamental chemical laws governing the observed pyrotechnic activities. In spite of the extensive use of pyrotechnic flares, tracers, signals, smokes, delays, incendiaries etc. in World War II and later, only the last two decades have seen attempts to understand and apply the laws of thermodynamics and the principles of solid state chemistry to explain the vagaries of pyrotechnic devices. The contributions of McClain¹ and Conkling² are noteworthy in this direction.

All the pyrotechnic devices function essentially on reactions between an oxidizer and a fuel. The reactions are invariably exothermic giving rise to a flame, smoke or

a trail in a controlled manner over a few milliseconds at the fastest range extending to several seconds or minutes. The main fuel - oxidizer reaction is suitably modified in a given device by the use of several other additives. The reaction can be represented as



where A is the solid fuel, B is the solid oxidizer (not necessarily an oxide), $A(O)_X$ is the product oxide of the fuel and D is the reduction products.

Elementary chemical principles dictate that

(a) the chemical nature of the fuel, (b) the chemical nature of the oxidizer, (c) average particle sizes and their distributions of the reactants, (d) the intimacy of mixing, (e) previous history of manufacture of the reactants (defect state), (f) conditions of storage of the reactants, (g) conditions of storage of the mixture prior to subjecting to the initiating impulse, (h) degree of confinement of the reaction mixture, (i) nature of modifiers or process aids used, (j) effective thermal dissipation from the reaction zone, (k) the temperature and pressure of the reaction, (l) the permittivity of the fuel oxide for diffusion of oxygen through the layer, (m) the mobility of the interface and finally (n) the enthalpies of reactions and the kinetic parameters of the various solid - solid and/or solid - gas reactions which take place should be considered in a rigorous treatment of modelling of the reaction.

It is indeed a formidable list of parameters for quantification. There is not a single pyrotechnic device for which all the above parameters have been fully defined. Therefore no single comprehensive theoretical treatment can predict the combustion characteristics of any pyrotechnic device with any degree of certainty with the result that even today pyrotechnic technology has remained more of an art than science. The devices and their applications being so diverse, several empirical equations have been proposed separately for each device or function which commence from squibs or flash cap upto the end result of a flare, signal, illumination or smoke through a series of delay trains, ignitors and so on. The relative importances of the parameters mentioned above, vary considerably in different applications and so afford credibility to the empirical equations developed specifically for a given function.

The difficulty in definition and characterization of the multicomponent solid - solid reactions arises primarily from a lack of definite information on the so called reaction temperature which can be precisely measured only in homogeneous systems. Due to inadequate dissipation of heat, the inside of the solid particles are generally at variance with the measured surface temperatures. The equations describing the kinetics of the reactions should take into consideration the varying temperature factor besides the geometrical and structural factors of the reactants and products. Isothermal methods have therefore limited applicability in solid - solid reaction. Most kinetic studies heavily depend on the non-isothermal methods which have found increasing

use in the understanding of pyrotechnic reactions, on account of the increasing sophistication in equipment and use of very small quantities of specimen. The small sample size has helped to achieve near homogeneous conditions.

All pyrotechnic reactions barring those in a few smoke compositions finally yield a combustion flame. The temperature of the flame and burning rates are determined by the thermodynamics and kinetics of combustion. Attempts have been made of late to correlate the kinetic factors and combustion rates and arrive at meaningful hypotheses on the course and extent of the reactions. Delay compositions and delay reactions have received the greatest attention as they are very vital in their functions while being relatively simple to study.

2. DELAYS

Pyrotechnic delays are introduced in ammunition, particularly in fuses to delay the terminal reaction by a predetermined interval. The delay could vary from a few microseconds as in the case of triggering devices to a few seconds as in signals and illuminating flares. The civilian explosive industry also uses several delay devices in blasting applications. The most common delay devices are the electric delay detonators which are used for controlled blasting to achieve better fragmentation, low ground vibration and less noise. Most commercial delay detonators are manufactured in two series, (a) milli second delay detonators and (b) half second delay detonators. The former are usually offered in nominal intervals of 20-25 milliseconds from a nominal zero to about 500 ms and at extended intervals thereafter. The latter series is offered with delay timings of multiples of 0.5 second upto 5 seconds. Some of the industrial compositions for millisecond delays are PbO_2 - Si , Pb_3O_4 - Si , Pb_3O_4 - Si - Sb_2S_3 , $BaCrO_4$ - PbO_2 - B . Half second delays are BaO_2 - Si , $KMnO_4$ - Sb , $BaCrO_4$ - Zr - Sb_2S_3 , Fe - $KMnO_4$ - PbO - Si , etc. The various oxidizers are Fe_2O_3 , PbO , Pb_3O_4 , PbO_2 , $KMnO_4$, Fe_2O_3 , KNO_3 , $K_2Cr_2O_7$, $PbCrO_4$, etc. Reducing agents are Si , Mn , B , Al , Mg , Sn etc. In delay composition, burning propagates by reignition from layer to layer along the burning path and therefore depends on the thermal conductivity of the mixture. Addition of inert materials reduce the rate of heat transfer through the mix and slows the reaction. Increased contact between reactants accelerate the solid – solid reaction due to diffusion in lattice components. Stoichiometry, heat of reaction and burning rate are interrelated.

Rees and co-workers^{3,4,5,6} have studied several aspects of the reaction of Si with PbO , PbO_2 and to some extent Pb_3O_4 binary systems employing DSC, DTA, bomb calorimetry and combustion rate measurements. It is to be noted, however, that the combustion of the fuel in a delay composition hardly ever goes to completion and therefore experimentally measured values are always subject to correction. Since ferric oxide is extensively used in several formulations of delay compositions. Some aspects of the work of Rees and co-workers by studying the effect of Fe_2O_3 in the red lead – silicon system employing DSC, DTA, hot stage microscopy and combustion rates has been extended.

3. MATERIALS

Pure red lead (Pb_3O_4) and silicon and analar grade ferric oxide (Fe_2O_3) were mixed homogeneously employing a wet mixing technique using a diatomaceous earth in water medium. This technique is similar to the method described by Mclain¹. Different particle size silicon i.e. 2μ , 5μ , 8μ were used to prepare the different compositions to study the particle size effect on the reaction mechanisms. The binder content was varied from 0 to 2 per cent. The compositions were dried and mixed homogeneously before loading into DSC or DTA instruments to avoid any agglomerations and inhomogeneity arising out of the difference in densities of the constituents. The compositions under study are given in Table 1.

Table 1. Composition of the samples prepared for the present studies.

Sample number	Red lead, Si, Fe_2O_3 weight proportion			Binder (%)	Particle size microns
	1	60	40	0	2
2	60	40	6	2	2
3	60	40	10	2	2
4	60	40	15	2	2
5	60	40	20	2	2
6	60	40	25	2	2
7	60	40	30	2	2
8	60	40	15		2
9	60	40	15	1	5
10	60	40	15	1	8
11	60	40	15	0	2
12	60	40	0	0	2

4. EXPERIMENTAL

Perkin Elmer DSC-2C instrument was employed to record the thermograms in nitrogen atmosphere in the temperature range 25 to 725°C. The sensitivity of the instrument was maintained at 10 mcal/sec. The sample mass was in the range of 2.5 to 6.0 mg.

DTA recordings were carried out using a home made Differential Thermal Analyser employing the Stanton Redcroft linear temperature programmer, a 610C Keithley Electrometer, a digital electronics two pen recorder and a self designed sample holder. Pt - Pt 13 per cent Rh thermocouples welded to the bottom of 99.99 per cent pure platinum cups were used. The sample cups made of platinum with 4 mm diameter and 3 mm depth were employed to keep the reference and sample

materials. -325 mesh tin metal powder was used for calibration. Thermograms were recorded in the temperature range 25 to 850°C and sample mass was varied from 18 to 60 mg.

The surface study of the pellets obtained from DTA experiment was carried out using an Orthoplan polarising Leitz microscope at 100 magnification.

A micro heating stage was employed to study the surface mobilities of the particles in the temperature range 25 to 1300°C along with the microscope.

Combustion rates were determined using a consolidation technique in lead tubes and delay timings were recorded in detonators.

5. DSC IN NITROGEN

DSC thermograms of sample 1 and sample 12 (Pb_3O_4/Si with and without binder) recorded in N_2 atmosphere are shown in Fig. 1. Two exotherms are observed with peak temperatures at 480 and 607 and at 503 and 613°C for the samples 12 and 1 respectively. A clear first peak is observed in sample 12 while the first exotherm

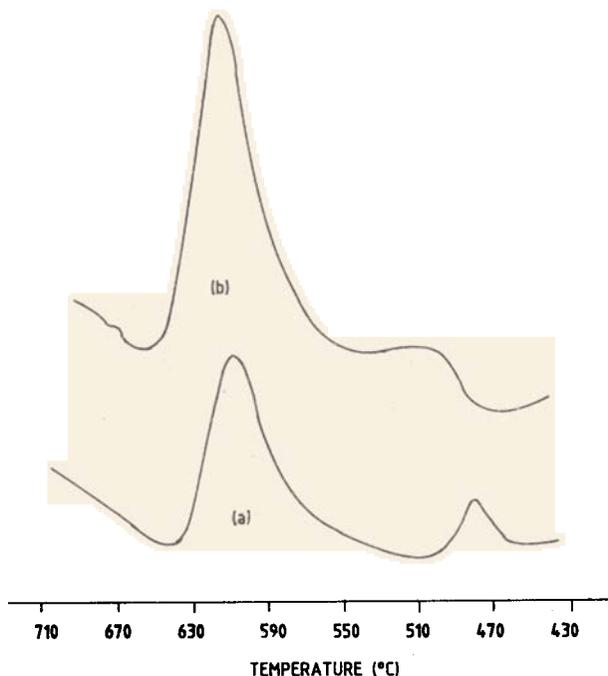


Figure 1. DSC of 60/40 (red lead/silicon) composition; (a) without binder, (b) with 2% binder.

appears as a shoulder in sample 1. The first exotherm peak temperature shifts to higher temperature side with the binder. The binder holds the constituents and maintains homogeneous distribution of the reactants. The enthalpies of the first peak in the two samples are in close agreement. The first peak is attributed to migration of particles followed by sintering effects. In the sample 12, due to the absence of

binder, surface mobility can take place freely as evident from the sharpness of the peak. In sample 1, the binder prevents the migration of particles. But with the rising temperature, a slow migration process can take place and is evident with the broad shoulder type exotherm.

Second exotherm is intense and the main oxidative pyrotechnic reaction takes place in this temperature region. The second peak temperatures of the two samples are in close agreement along with the enthalpy values. This reaction seems to be independent of binder. Al-kazraji & Rees³ observed that decomposition of Pb_3O_4 starts at 540° C and reaches a peak followed by the reaction between PbO and Si forming SiO_2 and Pb in N_2 atmosphere. The second peak is attributed to the decomposition of Pb_3O_4 and oxidation of Si .

DSC thermograms were also recorded as a function of ferric oxide content in the basic composition 60/40 red lead and silicon mixtures. Three exotherms were observed in all the samples with ferric oxide. The enthalpy values are given in Table 2. The

Table 2. Calculated enthalpies from DSC study.

Sample number	Enthalpy values cal/g		
	first peak	second peak	third peak
1	2.62	49.38	
2	3.5	39.73	1.20
3	3.79	32.23	1.83
4	1.86	48.62	2.61
5	4.04	25.04	8.40
6	1.6	41.93	1.81
7	2.02	23.20	2.02
8	2.652	22.72	7.71
9	1.33	21.76	18.46
10	0.50	24.83	17.15
11	7.9	44.23	
12	6.34	49.59	

first two peaks are similar to the observations made in the absence of ferric oxide and can be attributed to the same reactions. A third peak around 670°C was observed with ferric oxide and is unaffected with higher proportions of ferric oxide. Though ferric oxide acts as a retardant in combustion phenomena, it can also act as an oxidizing agent. The third peak may be due to the completion of the reaction between PbO and Si or due to the reaction between ferric oxide and silicon through the surface layers of SiO_2 . As the temperature rises, the oxygen from the initial coating of silicon dioxide diffuses into the bulk material of the particles. The depletion of oxygen on the surface favours further reaction.

Al-kazraji & Rees³ observed that one exotherm appeared around 590°C in N_2 atmosphere for compositions below 70/30 red lead and silicon. No exotherm was observed around 670°C in these compositions. Above 70/30, an exotherm around 670°C was observed and was attributed to the bulk oxidation of silicon through SiO_2 layer. In another study Abdolsamad, et al.⁴ observed that the reaction between silicon and red-lead occurred at 630 and 700°C thereby showing a shift of nearly 30°C. PbO also oxidized at the same temperatures. These were oxidizer rich formulations.

In the present study, it is unlikely to expect exotherm around 670°C for 60/40 compositions without an additional oxidizer. In the composition 60/40 without ferric oxide, no exotherm was observed around 670°C as expected. But in the presence of ferric oxide, a third exotherm was observed around 670°C. So this exotherm must be due to the oxidation of silicon by ferric oxide.

The thermograms of 60/40/15 with 2 μ , 5 μ and 8 μ silicon are shown in Fig. 2. It can be seen that the first exotherm reduces in intensity with increasing particle size and forms as a broad shoulder for 8 μ silicon in the composition. There is a slight shift

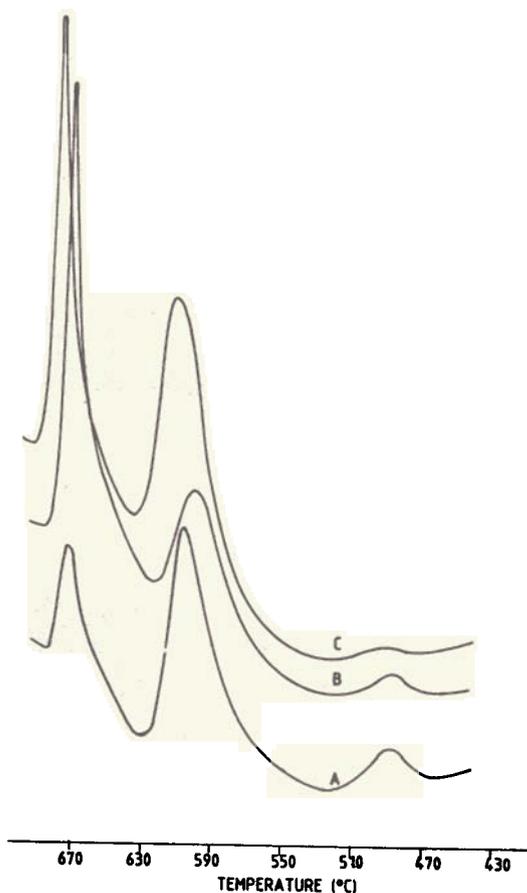


Figure 2. DSC of 60/40/15 (red lead/silicon/ferric oxide); (a) 2 μ , Si, (b) 5 μ , Si, (c) 8 μ Si.

of peak temperatures for 8μ silicon composition. The shift is however not very significant. The enthalpy values showed a decreasing trend for the first and third exotherms where as for the second exotherm remained almost same. A decrease in the enthalpy of the first exotherm is expected because of low exothermicities associated with the surface mobilities and sintering effects in compositions having low surface area. The second exotherm is due to decomposition of red lead associated with oxidation of silicon. The third reaction is due to the oxidation of silicon by ferric oxide through silicon dioxide. This main pyrotechnic reaction takes place at 570°C forming a silicon dioxide layer on silicon. Because of the large surface area available with the fine grade silicon (viz. 2μ) major part of the reaction is completed at this temperature and the subsequent bulk reaction by ferric oxide is unlikely to produce any large exothermicity. On the contrary, the coarser particles should show lower exothermicity at the first principally surface reaction and a sharp bulk reaction at the higher temperature. The experimental observations confirm this prediction.



Figure 3. DSC of 60/40/15 at different binder contents.

The binder effect on a single basic reactant composition is shown in Fig. 3. The first peak was shifted to higher temperatures i.e. 482, 490 and 496°C with 0, 1 and 2 per cent binder content. The other two peak temperatures are not affected significantly. The shift of the first peak to higher temperatures is easily due to the preventive barrier provided by the binder.

6. DIFFERENTIAL THERMAL ANALYSIS (DTA) IN AIR

DTA of $Pb_3O_4 - Si$ and $Pb_3O_4 - Si - Fe_2O_3$ mixtures prepared by wet mixing in the presence of a binder was recorded in air. The DTA of the base formulation namely 60/40 red lead and silicon is shown in Fig. 4. We find three exotherms centered around 560, 640 and 740°C for all sample sizes less than 20 mg. Rees, et al.³ have also made a similar observation. These three exotherms are attributed to surface reaction, bulk reaction and formation of a plumbate respectively. The compositions containing ferric oxide also show three similar exotherms around the same temperatures. Obviously these exotherms in the presence of ferric oxide must also due to the very same reactions. One important difference between the observations

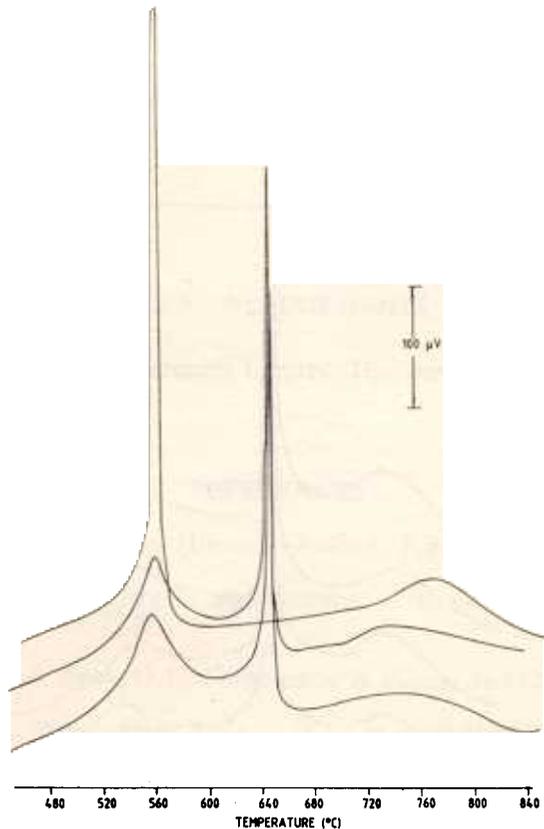


Figure 4. DTA in air of 60/40 (red lead/silicon) as a function of sample mass.

in nitrogen atmosphere and those in air is that the reaction temperatures have been shifted to lower values, which is expected in view of activation by the atmospheric oxygen. An important unusual observation shown in Fig. 4 is an abnormal high exothermicity of the first reaction as the sample mass goes beyond a certain critical value. In the case of all the compositions made with 60/40, 60/40/10, 60/40/20, and 60/40/25 we observed that a first reaction was largely intensified above a critical mass which was unique to each of the formulation.

The DTA of the samples above the critical mass invariably showed the absence of the second exotherm around 640°C. Any number of repetitions could reproduce the critical mass of a given formulation within ± 0.5 mg. This may be due to the fact that above the critical mass the sample attains such a high temperature that the second reaction is also completed due to the self-heating.

However in the case of samples made with 60/40/6 and those with 60/40/15 of different particle sizes and different binder proportions the first reaction was not enhanced at all (Fig. 5). These compositions also showed a critical mass, but the phenomenon was not as sharp as in the other cases. However the fact remains that the cause of enhancement of second reaction to criticality as against attainment of

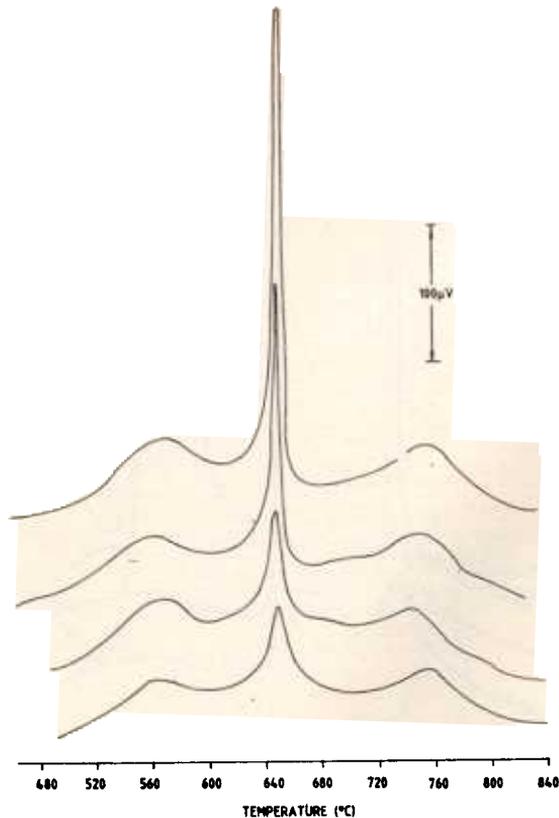


Figure 5. DTA in air of 60/40/6 (red lead/silicon/ferric oxide) as a function of sample mass.

criticality at the first stage itself with the other samples eludes a rational kinetic interpretation.

We have noticed that even in the second group of formulations the criticality could be reproduced within about 1 mg. The critical mass appears to increase with increasing binder content and likewise with increasing ferric oxide content. One could reasonably attribute the effect of the binder to heat transfer phenomena while the effect of ferric oxide is more likely to be due to relatively lower oxidative power of ferric oxide in relation to lead oxide. Such weak oxidative power of ferric oxide has indeed found an application in formulations of delay compositions. The reduction of enthalpy of the third exotherm from 227, 156, 55, 49, 17 and to negligible values for 0, 6, 10, 15, 20 and 25 weight proportions of ferric oxide content in the sample leads to the conclusion of inhibition effect by ferric oxide in the formation of plumbates. The decrease in the combustion rates with increasing ferric oxide content in the composition signifies its role as retardant (Table 3). In several delay devices ferric oxide is indeed used as an inhibitor.

Table 3. Combustion data of some compositions.

Sample	Burning rate sec/30mm
60/40/	240
60/40/10	385
60/40/20	664
60/40/30	1178

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