Using Magnetic Nano Ferrites to Alter the Ignition Time Delay of Shellac-based Pyrotechnic Igniter

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Abstract

Reduction in the ignition delay time (IDT) of shellac-based pyrotechnic igniter using different magnetic nano ferrite additives are studied here. Nickel-ferrite ($NiFe_2O_4$), Cobalt-ferrite ($CoFe_2O_4$), and Zinc-ferrite ($ZnFe_2O_4$) were used as nano additives to prepare 32 pyrotechnic compositions. Six weight percentages (wt%) of the additives were investigated for their effect on the IDT when they were added first replacing the fuel part, second replacing the oxidizer part. The incorporation of additives significantly reduced the ignition delay time of the base composition. The addition of 5.5% $CoFe_2O_4$ delivered the maximum decline in ignition delay time i.e. by ~67%. It was observed that the addition of additives at the expense of fuel produced the best results. Cobalt-ferrite, when added for 4% at the expense of oxygen reduced the ignition delay by~62%.

1 Introduction

Pyrotechnic igniters provide the initial heat energy for a composite solid propellant to initiate their combustion reaction. Combination or individual energy sources such as electrical, chemical, compression-induced, or laser are used to provide the initial activation for the pyrotechnic charge. Produced heat energy from the pyrotechnic charge is transferred to the main propellant grain surface through the high-temperature gases and hot particles, also giving the initial boost in the motor chamber pressure [1], [2]. The most used initiator setup is based on the bridge wire setup, in which the nichrome/tungsten wire is surrounded by the igniter charge. An electrical power source is used to heat the wire to provide the required energy for the ignition of the surrounding charge [3], [4]. The time interval between the point of the first signal for the initialization of the external power source to the point where the charge attains a self-sustained combustion without any further need for an external power source is considered the ignition delay time [5]. This delay includes the time needed for the wire to reach the appropriate temperature required for the ignition of the igniter charge with the available electric power rating [6].

Shellac is a large hydrocarbon, natural rubbery energetic binder, which has been used since the end of the 19th century due to low ignition delay and temperature, making it a potential binder for the energetic

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material [7]. Shellac has been used in different energetic compositions for different purposes such as in ignition fuse, and fuel/ binder compositions [8]. Ye. et. al., it was noted that the aluminum particles coated with shellac had a catalytic effect on the thermal decomposition of ammonium perchlorate [9]. Due to this, shellac has attracted many researchers to study its potential to challenge the commercially used pyrogen and pyrotechnic igniters. Its energy output and thermal performance can be enhanced by using appropriate additives and catalysts. One such catalytic additive is iron (II, III) oxide (Fe_3O_4).

Metals ferrites are produced by removing the Fe ion from the Fe_3O_4 molecule and replacing it with a suitable metal. Most commonly, transition metals like Cobalt (Co), Nickel (Ni), Zinc (Zn), Manganese (Mn), etc. are preferred [10]. Due to their catalytic action towards high-energy fuels and oxidizer decompositions, ferrites are considered ideal candidates to be used as additives to alter the combustion and thermal characteristics of different energetic compositions [11], [12], [13], [14]. The present study aims to improve the ignition time delay of shellac and potassium nitrate-based pyrotechnic igniters by testing various wt% of different magnetic nano-ferrites synthesized with three transition metals as substituent ions.

2 Methodology

2.1 Material

Potassium nitrate (CDH, purity >99%), shellac flakes (make CDH, purity >98.99%), isopropyl alcohol (Quali techs, purity >99%), cobalt nitrate hexahydrate (Sigma Aldrich >99% purity), zinc nitrate hexahydrate (Sigma Aldrich >99% purity), nickel nitrate hexahydrate (Sigma Aldrich >99% purity), citric acid anhydrous (Qualigens, purity ≥ 99.5%) and iron (III) nitrate nonahydrate (Qualigens, purity > 99%) were commercially obtained for the study and were used without any further treatment.

2.2 Preparation

The nano-sized additives used were zinc-ferrite, nickel-ferrite, and cobalt-ferrite. These nano ferrites were synthesized and characterized by Thakur et al., using the conventional citrate precursor method for which the detailed procedure and schematics are described in ref [15], [16], [17]. These nanoparticles were subsequently used in our experiments without further modification. The pyrotechnic stars were prepared by following the procedure mentioned in the ref [18]. The powdered and sieved constituents were divided into two different groups. The particle size of shellac and potassium nitrate were kept below 75 µm. The shellac and potassium nitrate were mixed in a ratio of 1:4. The additives were added to the composition at a wt% ranging from 1% to 6% with a step increment of 1%. Two different types of compositions were prepared: one with the additives added at the expense of fuels and the second when the additives were added at the expense of oxidizer. Isopropyl alcohol was used as a solvent for shellac to prepare the energetic binding lacquer.

All the ingredients (shellac as fuel and binder, potassium nitrate as oxidizer, and nano ferrites as additives) for the composition were thoroughly mixed in a 50.0 mL glass beaker with 1.70 g of isopropyl alcohol, and the prepared propellant slurry was transferred to the plastic cylindrical tube with a barrel length of 9.0 cm and diameter of 1.5 cm. The plastic tube was open from one end and had a piston/plunger at one end. The open end was sealed using sealing tape. The whole setup was kept under 5.0 kg weight applied on the plunger for 30 minutes. This was done to ensure tight packing and uniformity in the microstructure and density of the composition throughout the whole length of the tube. The cast sample was then pushed out of the tube using the plunger and cut into 4 pieces of length 2.0 cm each, using a Surgical #10 disposable blade scalpel. The samples were then left to be cured at NTP conditions for another 96 hours. This would allow the isopropyl alcohol to vaporize. The cured samples were then placed in a desiccator with $CaCO_3$ as a desiccant for another 24 hours, to remove any moisture that might have been absorbed during the open environment curing period. Figure 1 presents the prepared pyrotechnic igniter samples with nichrome wire pierced through the center of the bead.

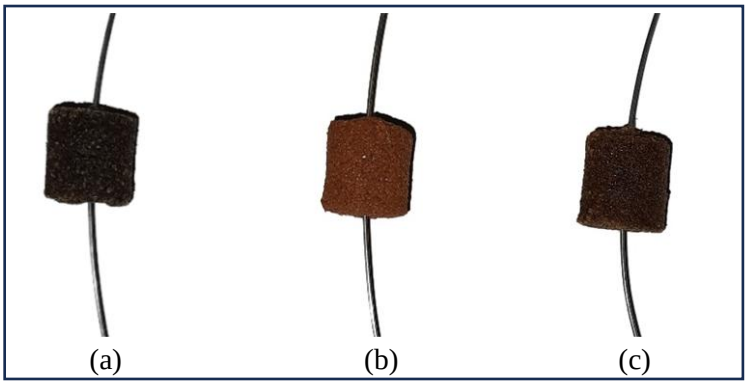


Figure 1. Prepared pyrotechnic igniters with (a) $CoFe_2O_4$ (b) $ZnFe_2O_4$ (c) $NiFe_2O_4$

2.3 Experimental setup an ignition time delay testing

Figure 2 represents the circuit diagram for the actual hand-held device fabricated to test the ignition time delay for the prepared pyrotechnic composition. All the samples were pierced with a nichrome wire of 6.0 cm and a diameter of 0.62 cm. Battery with a power rating of 12 V and 7 Ah was used to provide the electrical energy for the joule heating of the ignition wire.

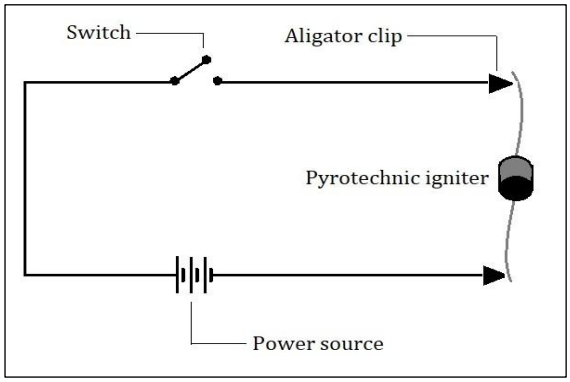


Figure 2. Line diagram of the Igniter setup

Eight samples of each composition were tested under an open environment inside a fume hood to investigate the average IDT. An open environment was chosen for the test to replicate the initial phase of the rocket launch process where the chamber conditions are at equilibrium with the atmospheric conditions. The whole process from initialization of the signal to the point where a sustainable combustion of the pyrotechnic charge was video-recorded using a high-definition camera at 60 frames per second. This video was watched at a playback speed of 0.5X to obtain the time lack between the above-mentioned points of interest, and the IDTs were calculated.

3 Results and discussions

Nano ferrites of Zinc, Nickel, and Cobalt were used as additives to alter the thermal behavior and IDT for the shellac and potassium nitrate-based pyrotechnic igniter. The values of IDT for 1% - 6% of additives were obtained experimentally, whereas the values for the wt% that are multiple of 0.5%, were obtained numerically using Newton Rapson's forward interpolation method. The ignition time delay along with the standard deviation for all compositions with additives incorporated at the expense of fuel and oxidizer are tabulated in Table 1 and Table 2 respectively.

Table 1. Ignition delay time for base igniter composition and igniter composition with additives (at the expense of fuel) with standard deviation

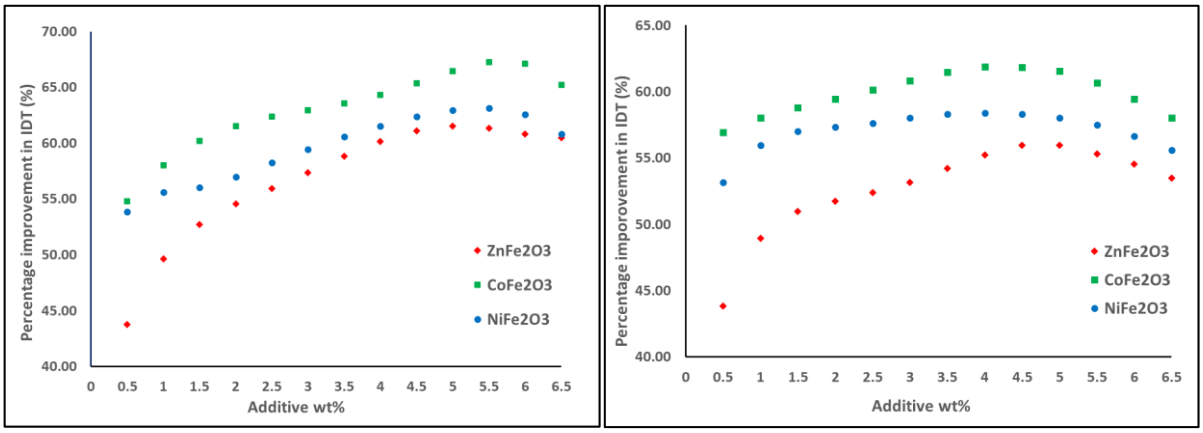
wt%	Zinc ferrite		Cobalt ferrite		Nickel ferrite	
	IDT (s)	Stand. Dev	IDT (s)	Stand. Dev	IDT (s)	Stand. Dev
Base	***1.43***					
0.5	0.804	0.0198	0.646	0.0232	0.660	0.0245
1	0.720	0.0268	0.600	0.0154	0.635	0.0130
1.5	0.676	0.0178	0.569	0.0223	0.629	0.0367
2	0.650	0.0256	0.550	0.0156	0.615	0.0323
2.5	0.630	0.0163	0.538	0.0232	0.597	0.0098
3	0.610	0.0206	0.530	0.0123	0.580	0.0251
3.5	0.589	0.0089	0.521	0.0143	0.564	0.0276
4	0.570	0.0142	0.510	0.0087	0.550	0.0135
4.5	0.556	0.0156	0.495	0.0154	0.538	0.0354
5	0.550	0.0146	0.480	0.0243	0.530	0.0275
5.5	0.553	0.0288	0.468	0.0145	0.527	0.0320
6	0.560	0.0209	0.470	0.0205	0.535	0.0120
6.5	0.565	0.0162	0.497	0.0276	0.560	0.0084

Table 2. Ignition delay time for base igniter composition and igniter composition with additives (at the expense of oxidizer) with standard deviation

wt%	Zinc ferrite		Cobalt ferrite		Nickel ferrite	
	IDT (s)	Stand. Dev	IDT (s)	Stand. Dev	IDT (s)	Stand. Dev
Base	***1.43***					
0.5	0.803	0.0174	0.616	0.0126	0.670	0.0174
1	0.730	0.0266	0.600	0.0244	0.630	0.0147
1.5	0.701	0.0168	0.589	0.0228	0.615	0.0156
2	0.690	0.0246	0.580	0.0242	0.610	0.0152
2.5	0.681	0.0168	0.570	0.0148	0.606	0.0243
3	0.670	0.0246	0.560	0.0247	0.600	0.0287
3.5	0.655	0.0134	0.551	0.0123	0.596	0.0094
4	0.640	0.0141	0.545	0.0212	0.595	0.0145
4.5	0.630	0.0275	0.546	0.0254	0.596	0.0154
5	0.630	0.0235	0.550	0.0113	0.600	0.0075
5.5	0.639	0.0288	0.562	0.0215	0.608	0.0127
6	0.650	0.0249	0.580	0.0205	0.620	0.0202
6.5	0.665	0.0172	0.600	0.0176	0.635	0.0194

The IDT for the base composition was 1.43 seconds. The percentage reduction in the IDT of shellac-based pyrotechnic igniter with different additives is illustrated in Figure 3. It can be seen clearly that the IDTs for the additively enhanced pyrotechnic stars were lower compared to the base composition. Comparing the reduced IDTs for compositions where the additives were incorporated at the expense of shellac to that of the samples where the additives replaced the oxidizer content, the former compositions show a better improvement in the ignition time delay. The incorporation of additives reduced the IDT for the igniter composition can be attributed to the fact that the amount of shellac reduced as the wt% of

additives increased, which in turn increased the available energy required to initiate the decomposition of leftover shellac molecules. Also, ferrites are known for their catalytic potential to favor a faster reaction rate. Ferrites are oxygen carriers and combined with the catalytic reduction of the fuel, it can lower the IDT for the pyrotechnic charge [19], [20].



(a) (b)

Figure 3. Percentage reduction (improvement) in IDT when additives are incorporated (a) at the expense of shellac (fuel) (b) at the expense of potassium nitrate (oxidizer)

The maximum reduction of 67% in IDT can be seen in the compositions when $CoFe_2O_4$ was incorporated at 5.5 wt% of the composition, at the expense of fuel content. It can also be seen that the IDT for samples where $NiFe_2O_4$ was added at the expense of oxidizer, is almost flat between the wt% of 1.5% to 4.5%. Furthermore, the best incremental improvement in IDT can be seen for the samples with $ZnFe_2O_4$. The maximum possible improvement in the IDT for $NiFe_2O_4$ and $ZnFe_2O_4$ when added at the expense of shellac is at 5.5% and 5% respectively. Similarly, when the additives are added at the expense of the oxidizer, the best improvement for IDT as seen for $CoFe_2O_4$, $NiFe_2O_4$, and $ZnFe_2O_4$ is 4%, 4%, and 4.5%, respectively.

Ferrites of different transition metals as substituent ions are known for their catalytic behavior to improve the thermal decompositions of different ionic oxidizers due to their ability to form Lewis sites leading to the formation of donor-acceptor relation as a part of Lewis interactions. It is also seen that the presence of nanometric ferrites of Co, Ni, and Zinc can accelerate the decomposition of major oxidizers by enhancing the decomposition rates of nitrogen oxides [21], [22].

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