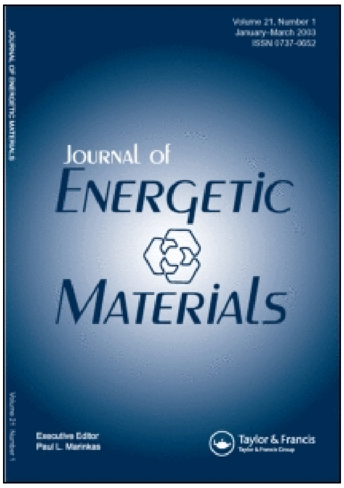

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Electrothermal Response and Functional Characteristics of Barium Ferrocyanide–Based Squibs

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In an attempt to replace toxic ingredients like lead ferrocyanide (LFCN) in electrical squibs, experiments were conducted by using barium ferrocyanide (BFCN) as an ingredient of squib composition. Electrothermal response (ETR), functional characteristics such as no-fire current (NFC) and all-fire current (AFC), were studied and compared with lead ferrocyanide-based squibs. Threshold firing currents were determined using the Bruceton staircase method. The squibs were also subjected to accelerated ageing and performance was evaluated. The results indicate better performance of barium ferrocyanide squibs to electrothermal response and a higher threshold no fire current, making it comparatively safe to handle as compared to lead ferrocyanide–based squibs. The results of accelerated ageing indicate a reasonable shelf life. ETR technique is found to be a good diagnostic tool for quality control.

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Keywords: accelerated ageing, electrothermal response, functional characteristics, quality control, shelf life, toxic, threshold no fire current

Introduction

Heat-sensitive ignition compositions are employed in the manufacture of bridge-wire–initiated electrical squibs (matches) and igniters to initiate an explosive train either in a pyro device or a rocket motor. It is well known that lead compounds and lead salts are widely used in pyrotechnic compositions, especially in squib, delay, and igniter compositions. When these compositions burn they produce lead-containing smoke, which is very toxic and also causes environmental and health hazards. Recommended exposure limit (REL) and permissible exposure limit (PEL), even as low as $0.05\,mg/m^3$ (as Pb), are toxic, as per NIOSH [1] standards, respectively. Hence it is required to explore the possibility of using lead-free compounds. With this view, a study was undertaken with barium ferrocyanide–based composition as a squib material. The PEL and REL limits for BFCN-based composition are $0.5\,mg/m^3$ (as Ba) [1] on a similar scale. Functional characteristics such as no-fire current (NFC) and all-fire current (AFC) were studied and compared with LFCN-based squibs. The results of firing currents were determined using the Bruceton staircase method. The squibs were also subjected to accelerated ageing and performance was evaluated.

Experimental

Bridge-Wire and Squib Plugs

Bare-bridged squib plugs were manufactured using nichrome wire 44 SWG [2] gauge. The squibs prepared have a resistance of 0.8 to 1.2 ohms. Barium ferrocyanide [3] $Ba_2Fe\,(CN)_6{\cdot}6H_2O$ of molecular weight 594 was prepared in-house using method reported in the literature. The barium ferrocyanide thus prepared has a purity of 98%, with Ba 44.6% and Fe 9.4%.

The average particle size was 3.7 µm with a density of 2.66 g/cc. Decomposition temperature of BFCN was 409°C determined using simultaneous thermal analyzer. Potassium perchlorate used was of purity of 98%, procured from M/s Wimco Ltd., Ambernath, Mumbai, with an average particle size of 5.3 µm and density 2.54 g/cc. Calcium silicide conforming to JSS specification [4] and particle size 10.5 µm was used and nitrocellulose-ammunition protective composition 217 was used as a binder.

Three batches (100 each) of squibs were prepared to determine the electrothermal parameters and functional characteristics (AFC and NFC) and one batch of 80 was prepared to study the effect of high temperature and high humidity on electrothermal parameters and functional characteristics.

Preparation of Squibs

Squibs were prepared by dipping the bare bridgedplugs in composition containing 40% barium ferrocyanide, 50% potassium perchlorate, 10% calcium silicide, and 2.5 parts NC binder. The charge weight of the spark-sensitive bead formed is about 30 mg. The bead is finally coated with NC lacquer to provide strength and water resistance.

Determination of Electrothermal Parameters

Various electrothermal parameters of the squibs were determined by electrothermal response (ETR) method [5–7] by passing a current of 350 mA for 300 ms. For this purpose, a computer-controlled non-destructive testing (NDT) instrument [8] was used. The instrument consists of: (a) a constant current pulser with adjustable current and pulse width, and (b) signal amplifier and one PC-compatible circuit for A/D conversion. The data acquisition was done by software developed in Turbo-C. A block schematic diagram of the experimental set up is given in Fig. 1. The data was displayed on the computer screen as voltage/time graph Fig. 2. The results are presented in Table 1.

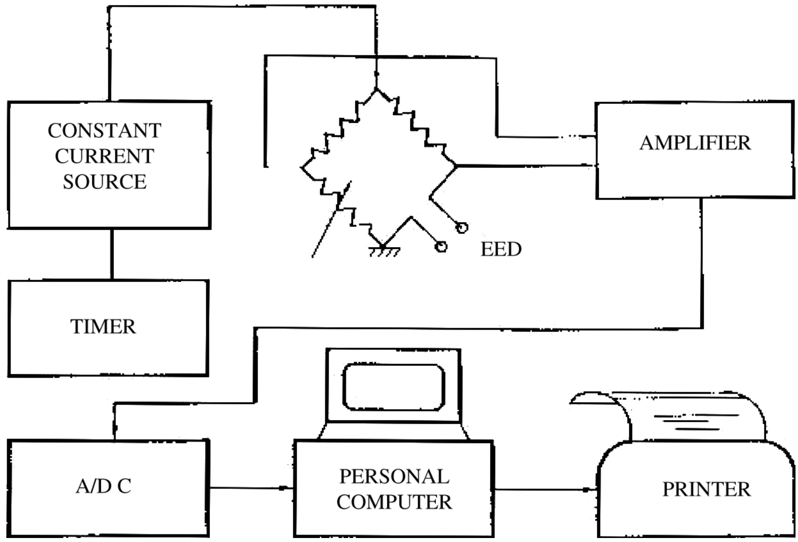

Figure 1. Block schematic diagram of NDT instrument.

Determination of Functional Characteristics (AFC & NFC)

All-fire current (AFC) and no-fire current (NFC) of the squibs were determined by the time-honored Bruceton staircase

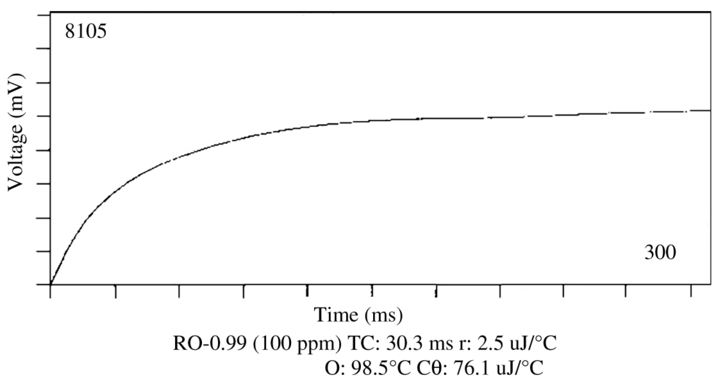

Figure 2. Time vs. voltage graph obtained from the NDT instrument.

Table 1
Electrothermal parameters of LFCN- and BFCN-based squibs

Parameter	LFCN squibs	BFCN squibs
Temperature spread* (°C)	18–97	24–70
Average temperature* (θ, °C)	43.6	40.4
Standard deviation	16.2	7.3
Squibs with temperature rise between 30 and 60°C (%)	55.0	93
Average heat capacity (Cp, μJ/°C)	88.1	82
Standard deviation	34.6	23.9
Average heat loss coefficient (γ, mW/°C)	3.5	3.2
Standard deviation	2.7	0.7
Average time constant (τ, ms)	28.3	26.3
Standard deviation	6.5	4.8

*Above ambient.
Test current: 350 mA; time duration: 300 ms.
Sample size: 300 each.

method, by using a transistorized power supply, model TSD-10 supplied by M/s Instrument Techniques Pvt. Ltd., Hyderabad. The results are presented in Table 2.

Table 2
Bruceton test results

Parameter	Lead ferrocyanide–based squibs	Barium ferrocyanide–based squibs
Average firing current (mA)	675	691
Standard deviation	77	30
N.F.C. (mA)	437	600
A.F.C. (mA)	913	785
Delay at 2 A (ms)	<20	<15

Sample size: 50 each.

Accelerated Ageing Study

Since adverse temperature and humid conditions lead to squib failures, studies were conducted at extreme temperatures and humid conditions.

1. Temperature: Accelerated ageing studies were conducted on 40 squibs at elevated temperature. The squibs were kept at 75°C for 15 days and then cooled to room temperature and electrothermal data generated by passing 350 mA current for 300 ms. The squibs were subjected to 3 such cycles (75°C for 15 days). After each cycle they were tested for electrothermal response. Results are presented in Table 3.
2. Humidity: 40 squibs were kept at 95% RH in a desiccator containing supersaturated solution of potassium sulphate for a period of 15 days. After removal, electrothermal data was generated by passing a current of 350 mA for 300 ms. The squibs were subjected to 3 such cycles (RH 95%, period 15 days). After each cycle they were tested for electrothermal response. The results are tabulated in Table 4.
3. Temperature and humidity: 40 squibs each were conditioned at 75°C for 45 days and at 95% RH for 45 days and then subjected to the following functional tests.

(a) Max. no-fire current: 10 squibs each, after exposure to high temperature and humidity, were tested by passing 500 mA current for 1 min. None of the squibs functioned.

(b) Min. all-fire current: 10 squibs each, after exposure to high temperature and humidity, were tested by passing 1 A current for 5 s. All functioned with a sharp sound and bright flash.

(c) Delay measurement: Delay of functioning was measured by passing 2 A current for 50 ms. 10 squibs each, after exposure to high temperature and humidity, were tested. All functioned with a time delay of less than 13 ms.

Table 3

Effect of high temperature (75°C) on electrothermal parameters of barium ferrocyanide–based squibs

Period →	Initial	After 15 days (1st cycle)	After 30 days (2nd cycle)	After 45 days (3rd cycle)
Parameter↓				
Temperature spread* (°C)	24–70	24–68	28–74	26–72
Average temperature* (θ, °C)	37.1	38.8	38.9	37.0
Standard deviation	9.1	9.3	9.4	8.8
Squibs with temperature rise between 30 and 60°C (%)	79.5	84.6	84.6	79.5
Average heat capacity (Cp, µJ/°C)	95.2	79.5	80.6	83.4
Standard deviation	29.9	14.9	70.1	18.6
Average heat loss coefficient (γ, mW/°C)	3.5	3.3	3.3	3.5
Standard deviation	0.8	0.7	0.7	0.7
Average time constant (τ, ms)	27.9	24.4	25.1	24.4
Standard deviation	7.5	5.4	5.6	5.9

*Above ambient.
Test current: 350 mA; time duration: 300 ms.
Sample size: 40 each.

Table 4

Effect of humidity (95% RH) on electrothermal parameters of barium ferrocyanide-based squibs

Period →	Initial	After 15 days (1st cycle)	After 30 days (2nd cycle)	After 45 days (3rd cycle)
Parameter↓				
Temperature spread* (°C)	29–82	26–81	25–81	26–83
Average temperature* (θ, °C)	49.4	45.9	43.8	45.7
Standard deviation	13.9	13.4	13.1	13.5
Squibs with temperature rise between 30 and 60°C (%)	80.0	83.0	80.0	83.0
Average heat capacity (Cp, μJ/°C)	81.5	69.6	71.8	67.3
Standard deviation	18.4	16.7	16.9	14.5
Average heat loss coefficient (γ, mW/°C)	2.7	2.9	3.1	2.9
Standard deviation	0.6	0.7	0.8	0.7
Average time constant (τ, ms)	31.1	24.9	24.4	29.9
Standard deviation	5.6	5.3	5.3	5.2

*Above ambient.
Test current: 350 mA; time duration: 300 ms.
Sample size: 40 each.

Results and Discussion

These results were compared with results of squibs containing 40% lead ferrocyanide 50%, potassium perchlorate, 10% calcium silicide, and 2.5 parts NC binder.

It is observed from the electrothermal response test results presented in Table 1 that the average temperature rise (θ°C) of the squibs is comparable. For squibs containing barium ferrocyanide the value is 40.4°C, while that for squibs containing lead ferrocyanide is 43.6°C. The number of squibs with temperature rise between 30 and 60°C for barium ferrocyanide fuel is 93%, while for squibs with lead ferrocyanide as fuel the number is only 55%. Squibs with barium ferrocyanide exhibited a narrow temperature spread of 24–70°C and low standard deviation of 7.36. In the case of squibs with lead ferrocyanide the temperature spread is wide, 18–97°C, and has comparatively high standard of deviation 16.2. Average heat capacity (Cp) of the squibs with barium ferrocyanide was 82.1 μJ/°C while with lead ferrocyanide fuel was 88 μJ/°C. A similar trend was observed with average heat loss coefficient (γ) and average time constant (τ). For squibs with barium ferrocyanide the heat loss coefficient and the average time constant is 3.2 mW/°C and 26.3 ms, respectively. However, standard deviation of 4.8 for the squibs with barium ferrocyanide is low compared to 6.5 exhibited by squibs with lead ferrocyanide.

Bruceton test results presented in Table 2 indicate that the squibs with barium ferrocyanide have threshold no-fire current of 600 mA, while squibs with lead ferrocyanide have low threshold no-fire current of 437 mA only. This is evident from standard deviation values of average firing current. Standard deviation for squibs with barium ferrocyanide is only 30, as compared to 77 for squibs with lead ferrocyanide.

During firing current determination, it was observed that all the squibs with barium ferrocyanide functioned instantaneously with a sharp report and a bright flash. Delay of functioning for squibs with barium ferrocyanide is less than 15 ms, while delay of functioning for squibs with lead ferrocyanide is less than 20 ms.

Results of accelerated ageing studies tabulated in Tables 3 and 4 indicate that there is no change in temperature rise, average heat capacity, average heat loss coefficient, or time constant, even after subjecting the squibs to elevated temperature at 75°C and exposure to 95% RH for a period of 45 days. It was also observed that there is no significant change in the functional characteristics of the squibs *viz.* maximum NFC, minimum AFC, and delay of functioning. These observations indicate that there is neither disturbance in the interface quality between the bridge-wire and squib composition, nor is there any performance degradation, suggesting a very good long shelf life.

Conclusion

- It is concluded from the ETR test results that the squibs with barium ferrocyanide are more uniform in nature and deliver the performance with close tolerances as compared to the lead ferrocyanide based squibs.
- Bruceton test results indicate that barium ferrocyanide based squibs exhibit a higher threshold no-fire capability of 600 mA, and therefore are comparatively safe to handle.
- Accelerated ageing results indicate that the squibs have a comparable shelf life.
- Barium ferrocyanide–based squibs are potential candidates to be used as an eco-friendly and safer substitute for lead ferrocyanide–based squibs.
- ETR technique is a useful diagnostic tool for quality control.

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