



# Cost-effective synthesis of 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14) and its evaluation in plastic bonded explosives

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Received 24 October 2002; received in revised form 27 May 2003; accepted 28 May 2003

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## Abstract

5,7-Diamino-4,6-dinitrobenzofuroxan (CL-14) has been synthesized by a cost-effective method. CL-14 was characterized by spectral data (IR, NMR and mass) and elemental analysis. The compound was evaluated in plastic bonded explosives (PBX) using polyurethane (PU) as binder. The thermal, mechanical and explosive properties of PBX composition from preliminary tests are also reported. Good thermal stability as well as good insensitiveness are indicated.

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*Keywords:* 5,7-Diamino-4,6-dinitrobenzofuroxan; Synthesis; Structural aspects; Polyurethane; Plastic bonded explosive; Thermal stability; Compressive strength; Explosive properties

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## 1. Introduction

The conventional explosive compositions based on 2,4,6-trinitrotoluene (TNT) are not suitable for bombs carried on high speed aircraft externally mounted and operated at lower altitude because of aerodynamic heating, which may raise the temperature of the fillings above 80 °C. Additionally, many ordnance systems are required to be safe if they are to be dropped from a considerable height or exposed to an accidental fire. Again, TNT based systems are not satisfactory [1,2]. The improvement of modern explosive charges to meet these requirements has taken two approaches : (1) synthesis of thermally stable, insensitive high explosive and (2) development of plastic bonded explosives (PBX).

The thermal stability of a molecule is achieved mainly due to introduction of amino groups into a nitro aromatic ring [3], condensation of nitroaryl halides with amino-triazole [4,5]

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or through the introduction of conjugation [6]. Further developments towards the production of explosives with low sensitivity and higher thermal stability have been made utilizing benzofuroxans, an extremely fruitful class of compounds for use as explosives. The furoxan ring results in increased density compared to nitro analogues whereas amino groups tend to reduce sensitivity as well as increase thermal stability and performance [7–9].

In order to increase thermal stability and invulnerability of the compositions a second approach has also been utilized; since PBXs have better heat resistance than melt-cast explosives. PBXs also have better mechanical strength, dimensional stability and cracking resistance [10]. In view of improvements in thermal stability and insensitivity, 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14) has been synthesized by a cost-effective method by modifying an earlier method of preparation [11]. In order to further increase thermal stability and low vulnerability of the composition based on CL-14, attempts have also been made to formulate a number of PBX compositions using polyurethane (PU) as binder and study their thermal, mechanical and explosive properties in detail.

In the following section of this paper, we report the low cost synthetic strategy and characterization of CL-14 followed by evaluation of thermal, mechanical and explosive properties of PBX compositions containing CL-14.

## 2. Experimental

### 2.1. Materials

4,6-Dinitrobenzofuroxan (DNBF) [12] (mp 173–74 °C), prepared in the laboratory from picric acid by treatment with pyridine followed by chlorination, azidation and pyrolysis, was used as our starting material. Polyurethane was obtained commercially from Uthane India Ltd., Chennai. Picric acid, pyridine, sodium hydrogen carbonate, hydroxylamine hydrochloride and methyl ethyl ketone, SQ Grade, were procured from Qualigens, Fine Chemicals, Mumbai while phosphorus oxychloride and sodium azide were procured from SD Fine Chemicals Ltd., Mumbai and used as such.

### 2.2. General methods

The melting point was determined using an open capillary tube. The IR spectrum was recorded utilizing a Perkin-Elmer infrared spectrophotometer employing a KBr matrix. <sup>1</sup>H NMR spectrum; the data were recorded utilizing a Bruker 90 MHz instrument. DMSO-d<sub>6</sub> was the solvent and tetramethyl silane (TMS) was an internal standard. Elemental analysis was performed utilizing a Carlo-Erba Elemental Analyser, EA 1108. The electron impact mass spectrum (EIMS) was recorded on a double focussing JOEL-DS mass spectrometer at 70 eV using direct insertion technique.

The deflagration temperature was determined using a Wood's Metal bath. The 0.02 g of sample was placed in a glass test tube and heated at a rate of 5 °C/min. The temperature at which the sample was ignited/decomposed was recorded as the deflagration temperature [13]. Differential thermal analysis (DTA) was performed using a 10 mg of sample in the presence of static air in place of the more usual flowing air to avoid oxidative degradation of

the composition on a DTA apparatus with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was carried out in platinum sample container using a Perkin-Elmer DSC-7. The 1.6–2.0 mg sample was heated at a rate of 10 °C/min. Thermogravimetric analysis (TG) was performed using the Mettler Toledo Star system by heating a 2–3 mg of sample at a rate of 10 °C/min. DSC, DTA and TG have been calibrated for temperature by using pure indium (In) and heat flow of DSC was calibrated by using specific heat method of sapphire over a user-defined temperature range. Vacuum stability was carried out by heating a 5 g sample in vacuum at 120 °C for 40 h, and measuring the total volume of gaseous products obtained at standard temperature and pressure.

Impact sensitivity was determined by Fall Hammer Method using a 2 kg drop weight. Friction sensitivity was determined utilizing the Julius Peter apparatus [14]. The velocity of detonation (VOD) was measured by using pin oscilloscopic method [15] and detonation pressure (DP) was calculated as per the reported method [16].

### 2.3. Synthesis of 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14)

4,6-Dinitrobenzofuroxan (5.0 g, 22.12 m mol) followed by addition of 100 ml distilled water were placed in a three-necked round bottom flask with a stirrer and dropping funnel. To the reaction mixture, sodium hydrogen carbonate (10.0 g, 119.04 m mol) and hydroxyl amine hydrochloride (6.0 g, 86.33 m mol) were added and the resulting reaction mixture stirred at 25 °C for 3 h. After this time period, the reaction mixture was cooled to 0 °C and pre-cooled 4N sodium hydroxide solution (100 ml) at 0 °C were added. The mixture was further stirred for 3 h. The yellow product thus obtained was filtered, transferred to a 1N hydrochloric acid (100 ml) solution and further stirred for an additional 1 h. The dark yellow precipitate thus obtained was filtered and washed thoroughly with water till it became acid free. The product was boiled with acetone to remove any adhering impurities and finally crystallised from dimethyl formamide, yield, 3.0 g (53%) mp 290–91 °C (decomposition), DTA 291 °C (endo followed by exo), IR (KBr)  $\text{cm}^{-1}$ : 3352 and 3246 ( $\text{NH}_2$  asym and sym str.), 1625, 1510, 1295, 1248 (furoxan ring), 1604 ( $-\text{C}=\text{C}-$  str), 1554 and 1346 ( $\text{NO}_2$  asym and sym str.) 1210 ( $\text{C}=\text{N}$  str).  $^1\text{H}$  NMR (DMSO- $d_6$ /TMS)  $\delta$  ppm :10.2 (s, br, 2H,  $\text{NH}_2$ , C-5), 9.6 (s, br, 2H,  $\text{NH}_2$ , C-7) EIMS (70 eV),  $m/z$ : 257 ( $m + 1$ ), 256 ( $M^+$ ), 240 ( $M-\text{O}$ ), 226 ( $M-\text{NO}$ ), 210 ( $M-\text{NO}_2$ ), 196 ( $M-2\text{NO}$ ), 180 ( $M-\text{NO}-\text{NO}_2$ ), 163 ( $M-\text{NO}_2-\text{HNO}_2$ ), 150 ( $M-2\text{NO}-\text{NO}_2$ ), 134 ( $M-\text{NO}-2\text{NO}_2$ ), 104 ( $M-2\text{NO}-2\text{NO}_2$ ).

Anal. calcd. for  $\text{C}_6\text{H}_4\text{N}_6\text{O}_6$  ( $M_w$  256): C 28.02; H 1.45; N 32.72%. Found: C 27.74; H 1.39; N 32.54%.

### 2.4. Preparation of PBX composition CL-14/PU (95/5)

To a steam jacketed stainless steel vessel (capacity 2.0 l) fitted with condenser, mechanical stirrer and dropping funnel, 95 g of CL-14 (prepared as above) was transferred carefully. Distilled water (1000 ml) were also added to the flask. The slurry thus obtained was warmed using steam to 60 °C with continuous stirring. At this stage polyurethane (number average  $M_w$  2200–2250) lacquer (prepared by dissolving 5 g of PU in 100 ml of methyl ethyl ketone) were slowly added through dropping funnel over 30 min. After the addition of PU lacquer, the whole slurry was stirred vigorously (500–550 rpm) for approximately for 30 min in

order to maintain uniform dispersion of the binder over CL-14 crystals. The solvent was then recovered by distillation. The vessel was cooled by passing cold water through it. The granulated PBX material was filtered and washed thoroughly with water and dried at 60 °C for 24 h in a water jacketed oven. The other two compositions, i.e. CL-14/PU (90/10) and CL-14/PU (85/15) were also prepared by similar procedure [17].

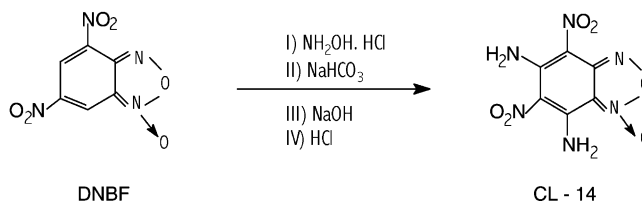
### 2.5. Determination of compression strength of PBX composition

The compression strength of the PBX composition was determined by pressing the pellet using a single action technique, in which weighed quantities of moulding powders were transferred to a 30 mm mould which was kept under hydraulically operated ram at ambient temperature. The applied force was  $\sim 1.7$  t/cm<sup>2</sup> pressure and dwell time 12–15 s. A “Universal Instron”, Model 1185 at constant speed of 50 mm/min was used. The results reported here are mean value of five crushed pellets.

## 3. Results and discussion

### 3.1. Synthesis and structural aspects

5,7-Diamino-4,6-dinitrobenzofuroxan (CL-14) was prepared from 4,6-dinitrobenzofuroxan (DNBF) by a modified method as outlined further.



DNBF was prepared from picric acid on treatment with pyridine followed by chlorination using phosphorus oxychloride. Azidation of chlorinated product and subsequent cyclization produced DNBF [12] which, on amination through “Vicarious Nucleophilic Substitution” using hydroxylamine hydrochloride and sodium hydrogen carbonate resulted in CL-14 with good yield and excellent product purity. The modified methods of amination not only enhanced the yield of CL-14 but also is four times less expensive as compared to previously reported method [11]. The low cost of synthesis of CL-14 is due to cheap and indigenously available  $\text{NaHCO}_3$  in place of using costly imported  $\text{KHCO}_3$ . Also, the yield of CL-14 is about 53% against 29% obtained from the reported method. The structure of CL-14 was confirmed by spectral data (IR, NMR and mass) and elemental analysis data.

### 3.2. Thermal and mechanical properties of PBX formulations

The thermal and mechanical properties of PBX’s were evaluated. The data obtained are presented in Table 1. It is clear that CL-14 as well as three different PBX compositions based

Table 1  
Thermal and mechanical properties of CL-14 based PBXs

Properties	CL-14	CL-14/PU (95/5)	CL-14/PU (90/10)	CL-14/PU (85/15)
Melting point (°C)	289–91 (decomposition)	289 (decomposition)	288 (decomposition)	288 (decomposition)
Theoretical maximum density (g/cm <sup>3</sup> )	1.91	1.85	1.80	1.75
Experimental density (g/cm <sup>3</sup> )	1.91	1.54	1.49	1.44
TMD achieved (%)	–	83.24	82.77	82.28
Deflagration temperature (°C)	290	290	292	290
Differential thermal analysis (°C)	291	290	291	289
Differential scanning calorimetry (onset peak temperature) (°C)	289.3	289.1	290	290
Vacuum stability (5 g at 120°C for 40 h) (cc)	0.30	0.53	0.61	0.87
Compression strength (kg/cm <sup>2</sup> ) <sup>a</sup>	–	217.0	134.7	101.0
Compression (%)	–	4.6	5.0	5.76

<sup>a</sup> Means the resistance to forces tending to compress, shorten or crush.

on CL-14 deflagrate almost in the same range of temperature, i.e. 290–92 °C. This finding further confirms that thermal stability of these PBX compositions is totally determined by CL-14 present in the composition and the presence of polyurethane does not degrade the thermal stability. This conclusion is fully rationalised by DTA thermograms where corresponding exotherms were found in the range of 290–291 °C, respectively. The above data are further supported by DSC onset peak temperature values where CL-14 as well as CL-14 based PBX compositions exhibit almost the same thermal stability (289–289.3 °C).

The thermo-gravimetric analysis of CL-14 is presented in Fig. 1. It is clear from the thermogram that there is a linear mass loss of about 7.6% upto 232 °C followed by 69% mass loss between 232 and 307 °C. Further, there is a 92% mass loss between 307 and 392 °C. Above 392 °C, there is slow steady mass loss due to residual decomposition of the compound. Further, the thermogravimetric analysis curve of PBX samples shows that there is almost the same pattern of decomposition of all the three PBX compositions. The representative thermogram (Fig. 2) shows that there is a linear mass loss of about 5% upto 225 °C, followed by a sharp 78% mass loss between 225 and 285 °C. Above 285 °C there is a slow steady mass loss upto 604 °C, presumably due to the oxidation of the PBX. This study indicates that after coating with PU binder the nature of decomposition pattern of CL-14 does not change significantly and thermal decomposition pattern indicates that the binder does not degrade the base material.

The vacuum stability data reveal that all the PBXs have good stability under vacuum at 120 °C for 40 h. The gaseous products obtained are in the range of 0.56–0.89 cc for 5 g sample (maximum permissible limit 5 cc/5 g) inferring good compatibility of CL-14 with polyurethane binder. The experimental values of compression strength of PBXs at ambient

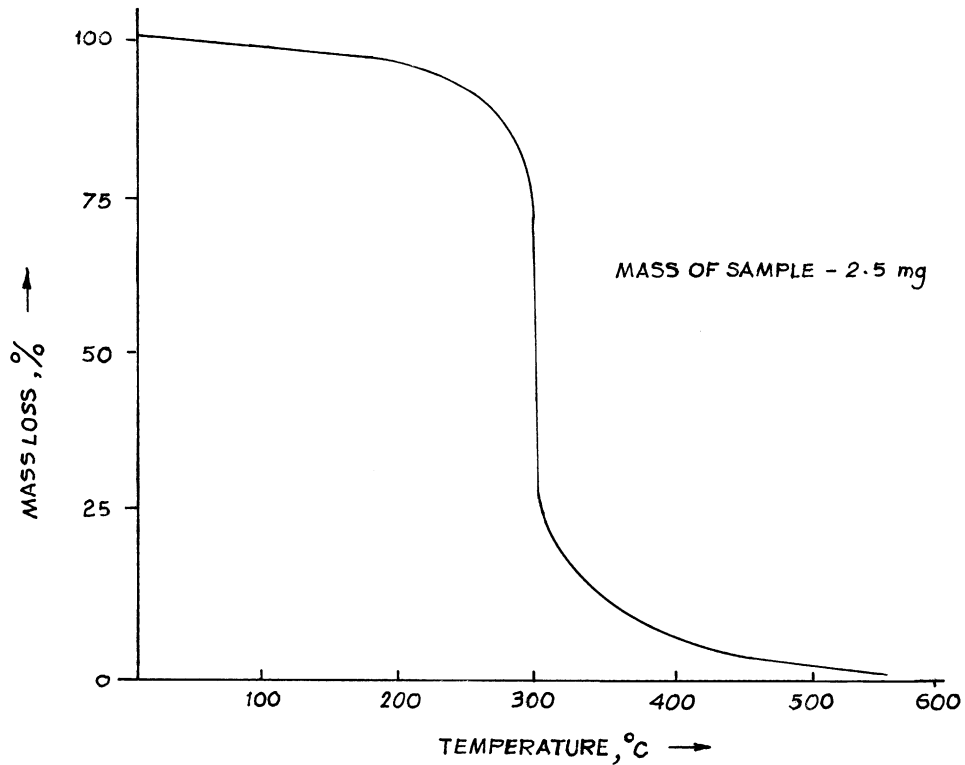


Fig. 1. Thermo-gravimetric curve of CL-14.

temperature are given in Table 1. It is evident that the compression strength of PBXs have a decreasing trend, i.e. CL-14/PU (95/5) > CL-14/PU (90/10) > CL-14/PU (85/15). This trend in mechanical strength agrees with the data generated for different binders, such as low density polyethylene (LDPE), ethylene-vinyl acetate (EVA), Viton-A, Kel-F 800 and Kraton G 1650 [18]. The decrease in mechanical strength is due to agglomeration of higher percentage of binders over the explosive crystals (confirmed by scanning electron microscope (SEM)) thereby bringing down the cohesive forces in the pressed pellets [19].

### 3.3. Explosive properties

The study on sensitivity and explosive properties (Table 2) of PBXs reveals that all the three compositions are quite safe regarding impact and friction forces. The insensitivity to impact increases with increased percentage of binder in PBX compositions. The VOD and DP of all the three compositions are given in Table 2. These data indicate at higher percentages of CL-14, VOD and DP are higher. This result is due to greater percentage of energetic material as well as density of pressed pellets which is achieved by better homogeneity of the formulation leading to good compactness of pellets during pressing.

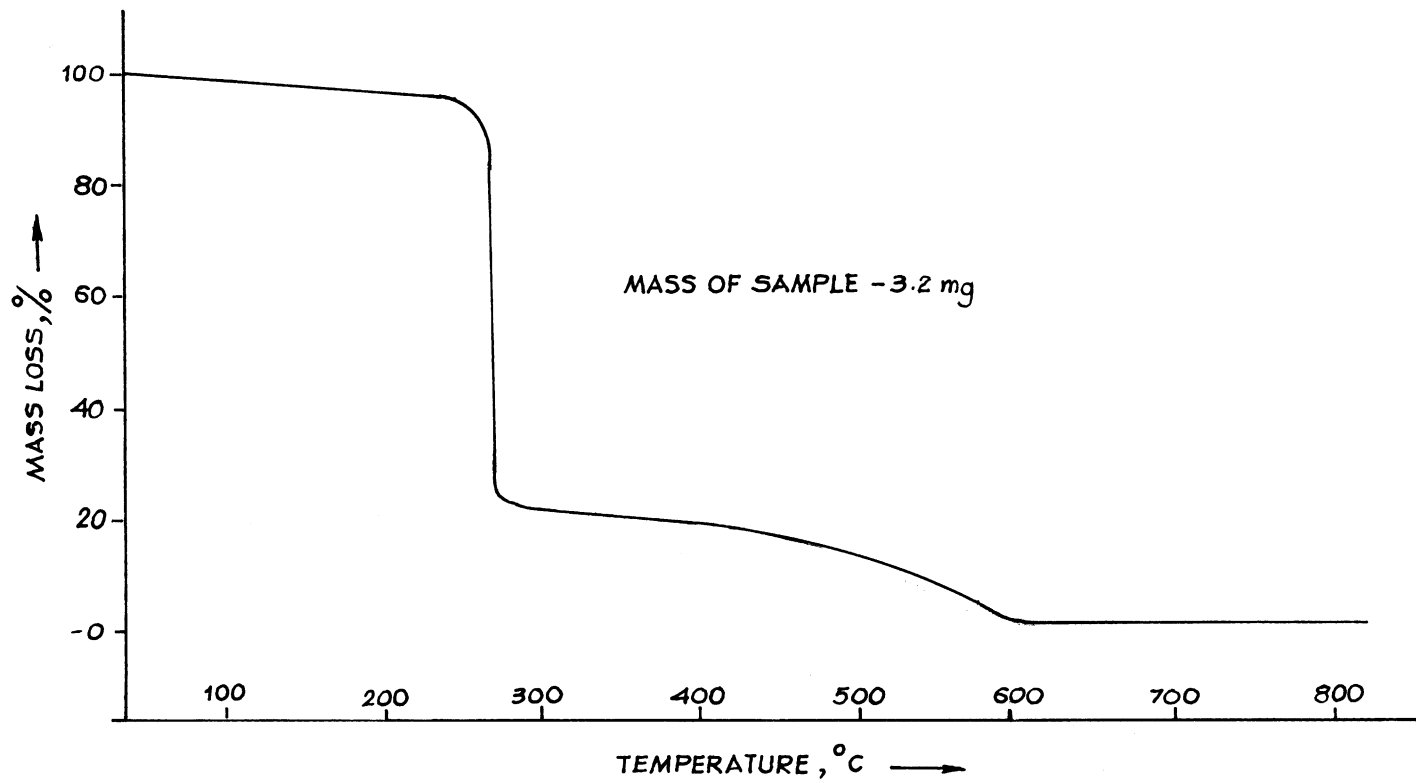


Fig. 2. Thermo-gravimetric curve of PBX based on CL-14/PU (85/15).

Table 2  
Sensitivity and explosive properties of PBXs

Properties	CL-14	CL-14/PU (95/5)	CL-14/PU (90/10)	CL-14/PU (85/15)
Experimental density (g/cm <sup>3</sup> )	1.91	1.54	1.49	1.44
Impact sensitivity (Ht. for 50% explosion) (cm)	94	105	120	130
Friction sensitivity (insensitive upto) (kg)	36	36	36	36
Velocity of detonation (m/s)	8340 (calcd.)	7235	7140	6915
Detonation pressure (kbar)	332.12	201.52	189.89	172.14

#### 4. Conclusions

5,7-Diamino-4,6-dinitrobenzofuroxan (CL-14) has been synthesized and characterized by modified cost-effective method. Our prime interest in performing this work was to explore the utility of CL-14 in low vulnerable explosives (LOVEX) where thermal stability coupled with insensitiveness are considered main objectives. Our results appear to be favourable in this regard.

#### Acknowledgements

The authors thank Dr. Haridwar Singh, Director, High Energy Materials Research (HEMRL) Laboratory, Pune and Dr. J.P. Agrawal, Associate Director, HEMRL for their support and encouragement during the course of this study.

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