Thermochimica Acta, 134 (1988) 419–428
Elsevier Science Publishers B.V., Amsterdam

A STUDY ON THERMAL BEHAVIOUR OF SOME COMMERCIAL EXPLOSIVES

MD.NABIULLAH , R.N.GUPTA , B.SINGH AND P.K.GANDOPADHYAY

1 Scientist, 2 Head Blasting Division, 3 Director,
Central Mining Research Station,Dhanbad,Bihar(India).
4 Asst.Prof.Indian School of Mines,Dhanbad,Bihar(India)

ABSTRACT

The types of commercial explosives commonly used in India for open pit and underground mining operations and excavation industry include NG based solid explosives, ANFO, slurries, emulsions and liquid oxygen. Problems encountered occasionally in open pit coal mines during blasting are hot hole conditions due to extraction of underneath coal seams in the past. In many cases coal was left in the worked out areas which subsequently resulted in fire. In India, there are about 40 odd coal mines on fire mainly near the out crop. Due to fire in coal the temperature of the over burden strata recorded was upto 300°C and at times more. The temperature of blast hole in fire areas was between 60°C and 600°C. Explosives are used in such conditions to remove the overburden rock after lowering the temperature. Blasting in hot holes is done with special approval from the statutory authorities. From the safety point of view it is important to study the thermal behaviour of explosives before using them for blasting.

The behaviour of an explosive where there is a possibility of slow thermal oxidation due to thermal conduction from the rock surrounding the combustion zone, depends largely on the nature of explosives, source, rate of heating, mode of heating, degree of confinement and quantity of explosives used.

Thermal behaviour of NG based (OCG), watergel (Al sensitized) and detonating fuse were investigated by the authors at different temperatures in unconfined, in steel pipe confinement and hot bore hole conditions. Lagging time, temperature of explosion and ignition temperature were recorded. Drop impact sensitivity at different temperatures was investigated. NG based explosives burnt in unconfinement but detonated in steel pipe and in hot holes under confinement at approximately 100°C. Water-gel explosives lost their gel structure at 80°C but no detonation was recorded in steel pipe confinement or in unconfined conditions.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

INTRODUCTION

In 1984 an accident took place in an open pit coal mine in which six miners were killed due to premature detonation of explosives(1) while working in hot over burden holes just above a worked coal seam which was on fire. The best way to control a coal mine fire is to extract the coal on fire after blasting the over burden rock above. For blasting in fire areas the explosives, detonating fuse and detonators are used at temperatures above ambient and under confined conditions. Information available in literature is scanty and does not throw any light on the thermal behaviour, mechanism of decomposition and explosive reaction of commercial explosives at elevated temperatures and confinements. Sato et al (1) studied heat resistance of dynamite and water-gel. The dynamite strated decomposition at 130°C and the slurries at 150°C. Andreev and others (2-6) investigated the effect of temperature on some explosive ingredients including TNT and NG but did not throw any light on the thermal behaviour of commercial explosives. Person (6) studied the heat of combustion and burning rate of blasting gelatine at pressures between 1 to 11 Kb/cm^2. Burning rate of explosive increased with the increase of pressure. RDX, HMX, PETN and tetryl detonated when burning rate exceeded 1 m/s in unconfined state (7). Yaoyama et al (8) reported that tetryl started decomposition at 90°C and exothermic reaction was recorded at 160°C. Chattopadhyay and Seshan (9) studied the heat precariousness of some commercial explosives and measured heat of reaction with the help of differential scanning calorimeter.

In the present investigation studies have been made on the thermal behaviour of NG based commercial explosives including OCG, detonating fuse and a few water gels at different temperatures to measure ignition and explosion temperatures. Detonating fuse burnt in unconfinement at 130°C and exploded in steel pipe confinement. However, the explosion was localised and was not propagated through the cord. OCG burnt at 120°C in unconfined condition. However, it also started burning when the full cartridge was heated at a temperature of 100°C for 2.5 hours. It also started burning after 15 min of dropping a full cartridge over a hot bed heated at 100°C. It detonated at 110°C under steel pipe and blast hole confinement. Aluminium sensitized watergel explosives lost their gel properties at 80°C and started decomposition at 150°C.

Scanning calorimetery curves of OCG watergel and ANFO explosives showed an exothermal reaction at 135°C, 150°C and 275°C.

EXPERIMENTAL SET UP AND RESULTS

The following investigations were carried out for the study of the thermal behaviour of explosives:

i. Drop test of explosives with detonating cord on hot surface

ii. Heat test of detonating fuse

iii. Thermal stability test of explosives

iv. Heat precariousness using differential scanning calorimetry and Arrhenius kinetic constants of OCG.

Drop test of explosive with detonating fuse on hot surface

A cement asbestos pipe of 1.8m length and 0.15m diameter was vertically fixed over a hot plate thus, simulating a blast hole. 0.4m column of the pipe over the hot plate was coiled with nichrome wire to act as a tubular furnace and to maintain a uniform hot condition. The arrangement is shown in Fig.1. A sand layer of 2 cm was spread over the hot plate. The temperature of hot plate/sand bed inside the cement pipe was measured by means of calibrated thermistors and thermocouples using a control switch to maintain the temperature.

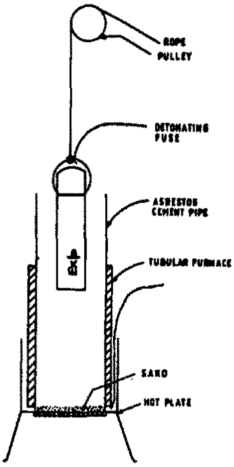


Fig.1 Arrangement for impact sensitivity test on hot surface

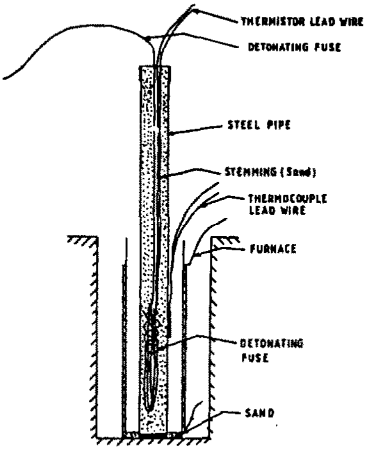


Fig.2 Arrangement for heat sensitivity test of detonating fuse

Explosives cartridges weighing approx.6.25 kg each were tied with detonating fuse 1.5 to 3.0 m above the hot surface and were dropped on the hot sand bed through a cement pipe using a pulley and rope. The dropped cartridges were allowed to remain in contact with hot sand bed for periods ranging between 3 min to 4 hours in order to study the behaviour of explosives under simulated borehole conditions. The experiment was repeated several times at different bed temperatures (70°,100°,120° and 150°C). Results are given in Table-1.

TABLE 1

Drop test of explosive tied with detonating fuse on hot surface

Sl. No.	Temp.of sand bed (° C)	Ht.of fall (m)	Observation	
			NG based	Slurry
1	70	3.0	No burning or explosion upto 4 hours	No burning or explosion.
2	100	3.0	Burning of explosive but no explosion after 15 min.	No burning or explosion upto 3 hours.
3	120	3.0	Burning of explosive with detonating fuse but no explosion after 3 min.	No burning.
4	150	3.0	Burnt but no explosion after 3 min.	Fumes but no flame after 30 min. but slowly burnt after 1 hour.

The information obtained in the thermal behaviour of detonating fuse and explosive under laboratory condition was tested in boreholes drilled in the rock at mine sites.

Heat test of detonating fuse

A tubular furnace of 0.5m length was placed vertically into a hole drilled in the rock at the mine site. Detonating fuse of 3.0m length was used for testing. A portion of detonating fuse was coiled and the coiled portion was hung inside the tubular furnace so that a small portion of the cord was outside the drill hole. The furnace was heated to investigate the behaviour of detonating fuse in unconfined condition. Cr/Al thermocouples were used to record the temperature .

Similar tests were repeated in steel pipe confinement. A coiled portion of detonating fuse was inserted inside a steel pipe with one end closed. The length of the steel pipe was 1.5m and the coil of detonating fuse was near the closed end. The steel pipe along with the fuse was filled with sand and a steel cap was screwed at the top end. The other end of the cord was taken out of the steel pipe through a small hole in the cap. The closed steel pipe containing the fuse was placed inside the tubular furnace and the whole assembly lowered in a hole below ground. Fig.2 shows the experimental set-up used for investigation. Results are tabulated in Table 2.

Thermal stability test of explosives

Furnace set up and method of temperature measurement were similar to that described earlier. Explosives cartridges were heated to different temperatures and the temperatures were kept constant for some time to observe

TABLE 2

Heat test of detonating fuse

Sl. No.	Sample	State of test	Temp. °C	Observation
1	Detonating fuse 3.0m length	Unconfined in the furnace	130+2	Portion of detonating fuse inside the furnace burnt and the portion outside the furnace was uneffected.
2	-do-	Steel pipe confinement with sand.	130+2	Bursting of the steel pipe at the position of detonating fuse coil. The coiled portion of fuse was consumed. The portion of fuse outside alongwith small length inside the pipe which was covered with sand remained uneffected.

the change in behaviour under unconfined condition. Results of investigation are described in Table 3.

For confined test, a steel pipe of 1.8m length with one end closed was used. Explosive was placed in the pipe near the closed end. Steel pipe with 6.25 kg cartridge was lowered into the cement asbestos furnace. Closed end of the pipe containing the cartridge was inserted inside the furnace. Explosive temperature in steel pipe and the furnace temperature were recorded simultaneously. For trials in hot holes an explosive cartridge tied with detonating fuse and Cr/Al thermocouple was placed in a tubular furnace and lowered into blast hole of 0.20m dia and 6m depth. Blast hole was stemmed with sand. Furnace was heated and explosion temperature was recorded. Experimental arrangement in unconfined and confined condition are shown in Figures 3 and 4. Results of investigations are given in Table 4.

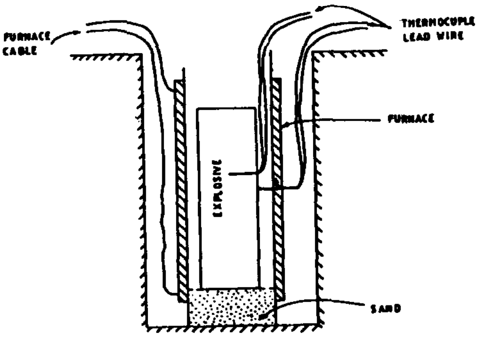


Fig.3 Arrangement for heat test in unconfined condition

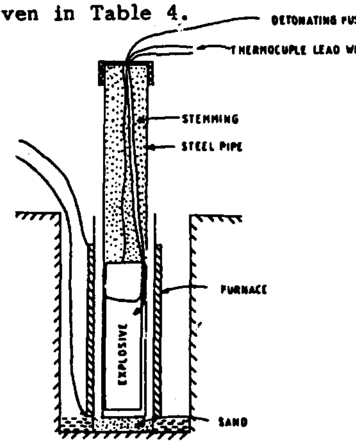


Fig.4 Arrangement for heat test of explosive in confinement

TABLE 3
Heat test of explosive

Sl. No.	Temp.of explosive °C	State of test condition	Time hrs. (h)	Observation	
				NG base(OCG)	Slurry
1	70	Unconfined	4	Sign of melting of PVC wrapper. Explosive was not effected	Cartridge wrapper melted.
2	90	-do-	3	Wrapper melted	Some liquid was separated from the gel.
3	100	-do-	2.5	Explosive started burning with flame	Liquid was separated but no burning upto 3 hours
4	120	-do-	-	Explosive started burning after 5 minutes	Gel structure destroyed, liquid boiled after one hour
5	130	-do-	-	Burnt	No burning but some fumes produce
6	150	-do-	-	-	Explosive started burning after 30 minutes
7	110	-do-	-	Explosive started burning with flame after 5 minutes	No burning upto 3 hours
8	110	Confined in steel pipe	-	Explosion of explosive which shattered the steel pipe	-do-
9	90	-do-	-	No explosion and no effect on pipe upto 3 hrs	-do-
10	130	-do-	-	-	No explosion

Heat Percariousness with DSC

Three types of explosives NG based, watergel (slurry) and ANFO were investigated using a Perkin-Elmer differential scanning calorimeter. Experiments were carried out using 20-26 mg of sample with nitrogen as the purge gas. Their ignition temperatures were recorded from DSC heating curves. Results are tabulated in Table 5 and shown in Fig.5.

Arrhenious Kinetic Constant

Experiments were conducted on DTA instrument type DT-30 Shimadzu (Japan) The rate of heating was between 2 and 20°C. The standard material used as reference sample was $\alpha Al_2 O_3$.

TABLE 4

Heat test of explosive tied with detonating fuse

Sl.	State of test	Temp.°C	Observation	
			NG based	Slurry
1	Unconfined in furnace	120+2	Explosive burnt but a portion of detonating fuse outside the furnace was uneffected. No explosion.	Boiled and gel structure destroyed No explosion
2	Confined with 0.5m sand stemming	120+2	Explosive burnt without ejection of sand stemming. A portion of detonating fuse outside was uneffected. No explosion.	burning/no explosion
3	Steel pipe confinement	110+2	Explosion with a loud, steel pipe was shattered to pieces, detonating fuse was fuly consumed	No explosion and fuse was uneffected
4	Blasthole confinement with sand stemming	110+2	Explosion with a loud, detonating fuse was fully consumed	-
5	Steel pipe confinement with sand	150	-	No explosion and detonating fuse outside the steel tube was uneffected but fumes were visible

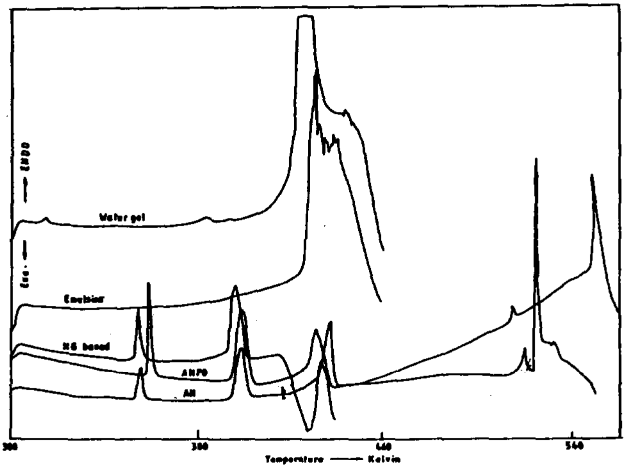


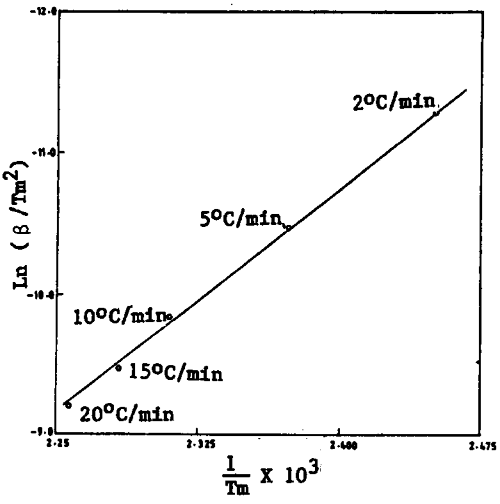
Fig.5 DSC heating curve of explosive rate of heating 8° K/min.

TABLE 5

Ignition temperature of explosives

Sl.	Explosive Name	State	Heating rate ° K/min	Ignition temp. ° Kelvin
1	AN	Powder	8	558
2	ANFO	-do-	8	543
3	OCG	NG base	8	415
4	KELVEX	Slurry	8	534
5	Power flo	-do-	8	534
6	PETN	Powder	8	425

Explosives weighing 40 mg were intimately mixed with 100 mg of αAl_2O_3 out of which 20 to 25 mg of the mixed sample was loaded into the sample cell. Result of investigation are summarized in Table 6. Using least square method of regression analysis between 1/Tm where, Tm is ignition temperature (Kelvin) of explosive and $\ln(B/Tm^2)$ where, B is rate of heating °C/min, the activation energy E and pre-exponential factor, Z, were computed as shown in Fig.6.



β= Heating rate (°C/min)

Tm=Reaction temp. (Kelvin)
Slope=d Ln (β /Tm²)/d (1/Tm)
E=Activation energy=21.27 KCal/mole.

Fig.6 Arrhenius Kinetic constant for thermal decomposition of OCG.

TABLE 6

Arrhenius Constant of NG based explosive

Name of explosive	B (°C/min)	Tm (Kelvin)	E (Kcal/mole)	Z (Mole/min/Kelvin)	Correlation coefficient
Open Cast	2	408	21.27		
Gelignite	5	421		5.83x10	-0.999
(OCG)	10	433			
	15	438			
	20	443			

DISCUSSION

It was observed that on heating NG based explosive in unconfined condition it started burning when the temperature was raised to 120°C but there was no detonation. The same behaviour of burning was exhibited at lower temperatures, 100°C, when the explosive was allowed to remain at that temperature for 2.5 hours in unconfined condition. It also burnt when the explosive was dropped from height of 3.0 m to a hot bed at 100°C and kept at that temperature for fifteen minutes. Detonation took place when the explosive was confined in a steel pipe in hot blast holes. In case of slurry explosives no detonation and or burning were observed in unconfined or in confined condition. However, their cap sensitive properties were lost due to loss of gel structure above 100°C.

In DSC plot of NG based explosives, in general, three endothermic peaks at 37°,80° and 120°C due to phase transitions of ammonium nitrate and large exotherm at 135°C corresponding to the thermal decomposition of the material with the evoluation of gaseous products were recorded. The thermal innitiation of explosion of OCG was contributed by multistage decomposition of ammonium nitrate where every single step caused instability of nitroglycerine. Isothermal study of explosive revealed that the thermal stability decreased at temperatures greater than 100°C.

Slurry explosives showed a slightly higher temperature of ignition than OCG. The ignition temperature varied between 155° to 175°C. Slurry explosives normally have the tendency to loose water and their gel structure above 80°C. Hence, many of the compositions showed large endothermic peaks and then the final decomposition peak.

The curve for ammonium nitrate and ANFO were of similar nature but decomposition temperature of AN was greater than for ANFO because the fuel oil which was used to sensitize AN lowered down the decomposition temperature of ANFO.

Thermal decomposition of PETN was also studied. It showed one endothermic peak at 135°C due to phase transition and melting and exothermic decomposition at 171°C.

ACKNOWLEDGEMENT

The authors are thankful to the staff members of blasting/explosive division and the IEL,Gomia for their co-operation. The views expressed are those of the authors and not necessarily of the institute to which they belong.

REFERENCES

1 R.N.Gupta,A.Bagchi and Md.Nabiullah et al "Some studies on sensitivity of open cast gelignite and detonating fuse and their behaviour in thermal condition. Internal Report of CMRS,Dhanbad(1985)

2 S.Sato,I.Tsubaki and T.Suenage, Journal of the Industrial Explosive Soc.Japan,38(1977) 286

3 K.K.Andreev,J.Applied chemistry,USSR, 31(1958) 984

4 K.K.Andreev, Explosives (1960) 54,102,167,241,275

5 G.B.Cook,6th International Symposium on combustion, Yale University (1956) 626

6 A.Person, Temperature change at exothermal decomposition NG,A.B. report(1959)

7 Griffiths and J.M.Cook, Journal of Chemical Society (1960) 4154

8 Griffiths and J.M.Cook, Explosives (1961) 276

9 Y.Yayama,S.Akihisa,S.Yoshitaka and E.Kitajema, Journal of the Industrial Society of Explosive, Japan,38(1977) 282

10 A.K.Chattopadhyay and S.Seshan, Fifth National Symposium on Thermal Analysis,IIT,Kharagpur Dec.20-22(1985)