THE CHEMICAL REACTIVITY TEST - A COMPATIBILITY SCREENING TEST FOR EXPLOSIVES

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ABSTRACT

   The chemical reactivity test is used to evaluate the compatibility of explosives with other materials. This test has been in use at Pantex for more than 15 years, and during this time several improvements have been made in the test apparatus.

   The basic test apparatus consists of a gas chromatograph with subambient temperature programming. A special inlet and a calibration system were designed and added to the chromatograph. Samples are conditioned in specially designed sample holders.

   A description of the test apparatus is given and data from a variety of different types of materials with explosives are discussed. Examples of various types of information which can be obtained from the test are also discussed.

DISCUSSION

   The chemical reactivity test[+] is an explosive compatibility test used to evaluate the stability of an explosive when in contact with another material. This test uses gas chromatography to identify, as well as measure, the amounts of decomposition gases evolved from heated samples.

   To evaluate the compatibility of a material with an explosive, samples of the explosive, the material, and a 50/50 mixture of the explosive and material are tested. Each sample is conditioned in a stainless steel container with a 103 to 138 kPa (15 to 20 psi) helium atmosphere at a constant temperature for a predetermined time (normally 120 C for 22 hours). At the end of the conditioning period, the gaseous products are analyzed by gas chromatography. Normally the gases measured are nitrogen, oxygen, carbon monoxide, nitric oxide, carbon dioxide, and nitrous oxide.

   At Pantex this test has replaced the vacuum stability test. The vacuum stability test is similar, but it only compares the total volume of gases

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[+]A New Explosive Compatibility Test, UCRL No. 6244, 1960.

from the explosive, the material, and a 50/50 mixture of the explosive and material. The test cannot distinguish such things as solvent and water vapors from decomposition products. Therefore, the chemical reactivity test gives a much more detailed analysis of complex decomposition reactions than the vacuum stability test.

The first CRT system used a 0.9 metre polypropylene glycol column to separate the more volatile reaction products from the water and solvents. Column number two was a 1.7 metre silica gel used to determine the nitrous oxide and carbon dioxide. A 0.9 metre Linda 5-A (molecular sieve) was used for a third column to determine the oxygen, nitrogen, nitric oxide, and carbon monoxide.

To simplify the operation of the three-column gas chromatography system the third column (Linda 5-A) was omitted and the 1.7 metre silica gel column was replaced with a 4 to 5 metre silica gel column. This two-column system would not resolve nitrogen from oxygen or carbon monoxide from nitric oxide, but it was successful with explosives systems containing HMX, RDX, TNT, and PETN.

To further simplify the operation and to increase the information from this test, a Porapak Q[+] column was used with subambient temperature programming. Using only a single Porapak Q column, it is possible to separate N_2, O_2, CO, NO, CO_2, N_2O, water, and a number of solvents. By using a standard two-column gas chromatograph, it is possible to simplify its operation and to obtain much more information about the chemical reactivity of the samples.

The chemical reactivity apparatus currently being used by the Development Division at Pantex is a Varian Model 1820-3 dual-column gas chromatograph equipped with a thermal conductivity detector and an automatic linear temperature programmer with the subambient temperature option.

It was necessary to add a special sample inlet system to the Varian gas chromatograph for the chemical reactivity sample holders. The sample inlet system was made from a Varian gas sampling valve. Fig. 1 is an illustration of the sample inlet system. This system is enclosed in a small oven and the line into the gas chromatograph is heated to keep less volatile products from condensing.

To simplify the calibration of the gas chromatograph, a manifold and another Varian gas sampling valve were added to the instrument as shown in Fig. 2. The volume of this valve was determined prior to calibration.

To calibrate the Varian gas sampling valve, a glass loop illustrated in Fig. 3 attaches to the chemical reactivity sample injection system. The volume of the glass loop was determined from the weight of the mercury required to fill the loop. Once the volume of the glass loop was known, it was filled with a gas
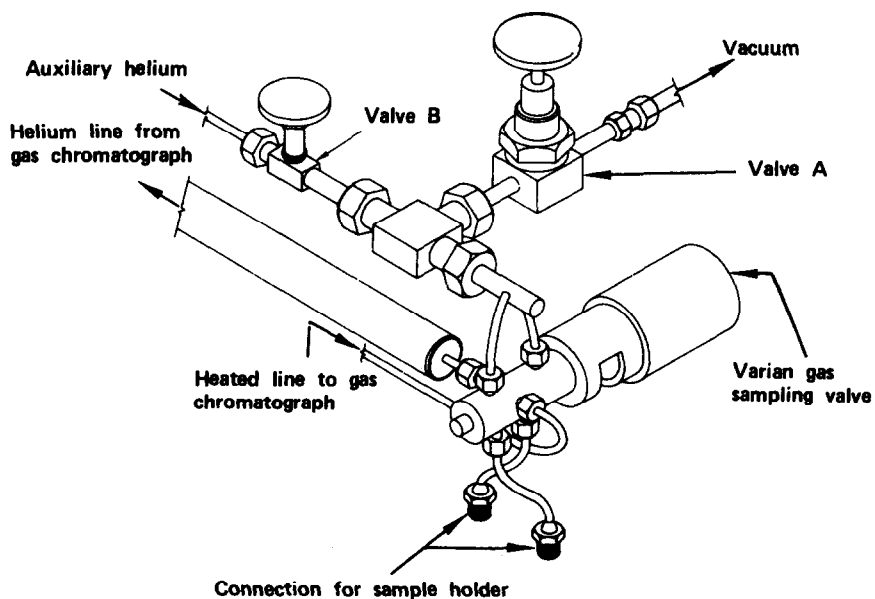
[+]Trademark of Waters Associates, Inc.

Fig. 1. Sample Injection Assembly

A - Helium Supply
B - Flow Controllers
C - Varian Gas Sampling Valve
D - Sample Injection System
E - Liquid Injection Ports
F - Columns
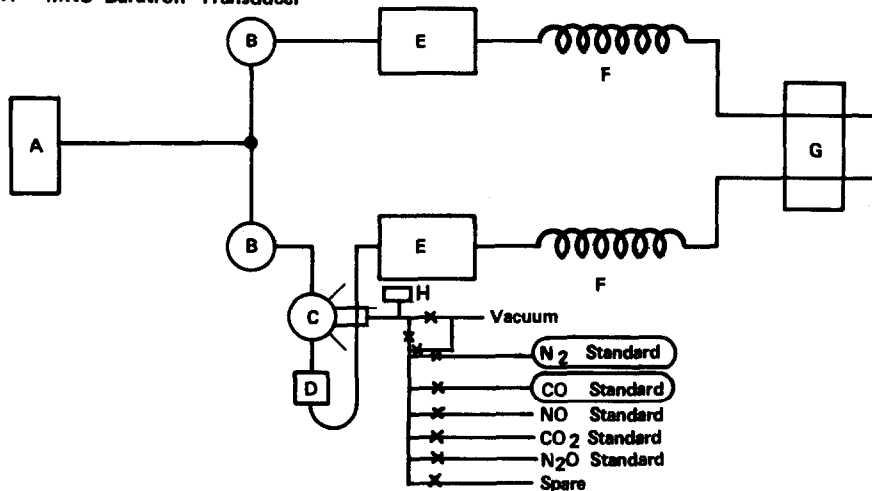G - Thermal Conductivity Dectors
H - MKS Baratron Transducer
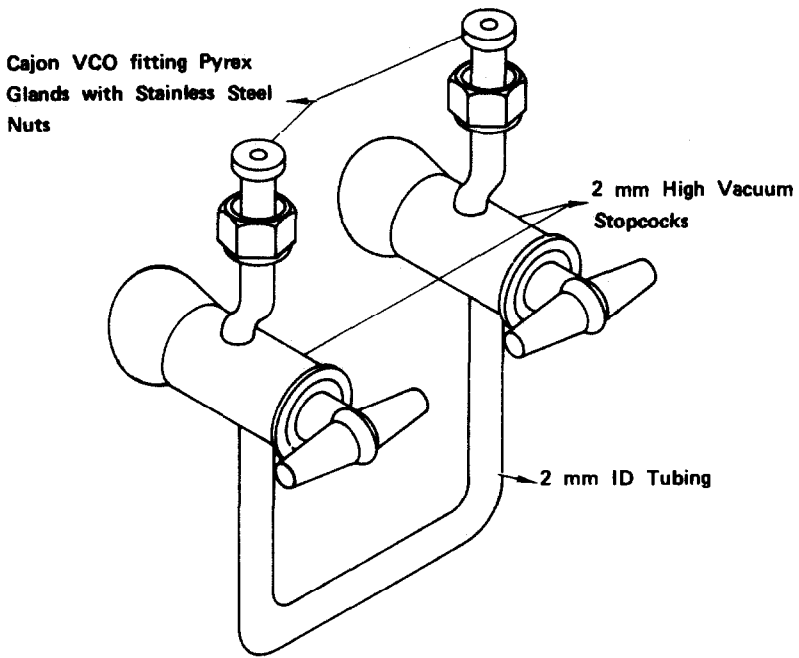

Fig. 2. Helium Flow Diagram for the Gas Chromatograph

Cajon VCO fitting Pyrex
Glands with Stainless Steel
Nuts

2 mm High Vacuum
Stopcocks

2 mm ID Tubing

Fig. 3. Glass Calibration Loop

Cajon 1/4-inch VCO

Whitey Series
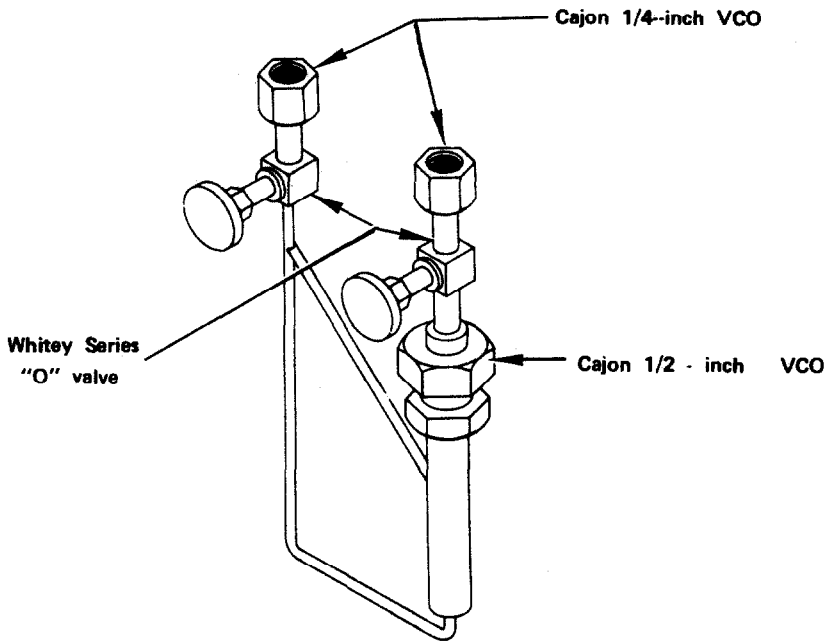 "O" valve

Cajon 1/2 - inch   VCO

Fig. 4. Chemical Reactivity Test Sample Holders

at a known pressure and temperature and injected into the gas chromatograph and a calibration constant calculated. The Varian valve was then used to introduce a sample of known pressure and temperature. By using the calibration constant determined with the glass loop, the volume of the Varian gas sampling valve was calculated.

The chemical reactivity sample containers were designed (Fig. 4) to obtain the best sample injection. These holders were made from stainless steel with all butt welds to eliminate any internal volumes which would slowly bleed the sample into the chromatograph. Stainless steel spacers are used in the sample containers to reduce internal volume.

Fig. 5 is a photograph of the chemical reactivity test apparatus used by the Pantex Plant Development Division Laboratories.
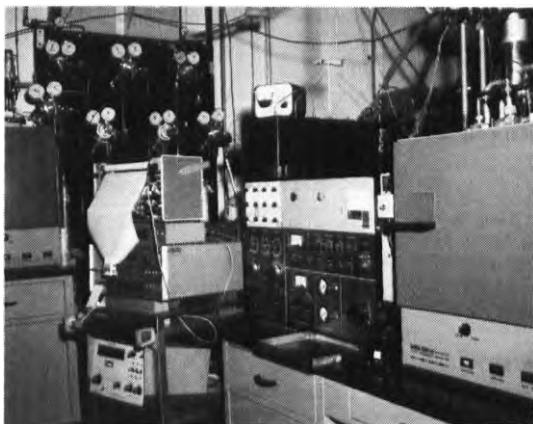

Fig. 5. Chemical Reactivity Test Apparatus

The following sequence is used to inject a sample into the chromatograph:

1. The sample holder is attached to the injection assembly (Fig. 1) which is in the sample position.

2. Then valve A is opened and the lines between the injection assembly and the sample container valves are evacuated to the desired pressure with valve B closed.

3. Valve A is closed and then valve B is opened and the evacuated volume is pressurized with helium to equal the pressure in the chromatograph. This eliminates a baseline shift due to any change in pressure in the instrument. Valve B is closed.

4. The gas sampling valve is then switched to the "inject" position and the sample container valves are opened.

The operation conditions for the chromatograph are:

Helium flow rate	30 cc/min
Column Porapak Q	4.5 m
Initial Temperature	-100 C
Final Temperature	200 C
Heat Rate	10 C/min
Holding Time at Maximum Temperature	30 min

The examples that follow illustrate typical data obtained with the chemical reactivity test apparatus, as well as data from a special investigation which show some of the additional information which can be obtained from the instrument.

The CRT chromatogram of LX-13 (Fig. 6) is given to illustrate the separation of the decomposition products. Since nitrogen and oxygen are separated, the oxygen can be used to determine if the sample holder leaked. Peak No. 8 is MF Freon which was used in processing LX-13. Peak No. 9 is acetone which is trapped in the PETN crystals during recrystallization.

The chromatogram (Fig. 7) of the double based propellant AHH illustrates how this system can separate other compounds.

The degree of reactivity of an explosive with another material is determined by the ratio of the volume of gas evolved by the mixture to the sum of the volumes of gas evolved by each component. The greater this ratio, the greater the reacti-

Milliliters of gas corrected to STP

1 - N_2 ------------ .008
2 - O_2 ------------ Trace
3 - CO ------------ .003
4 - NO ------------ .001
5 - CO_2 ------------ .007
6 - N_2O ------------ .002
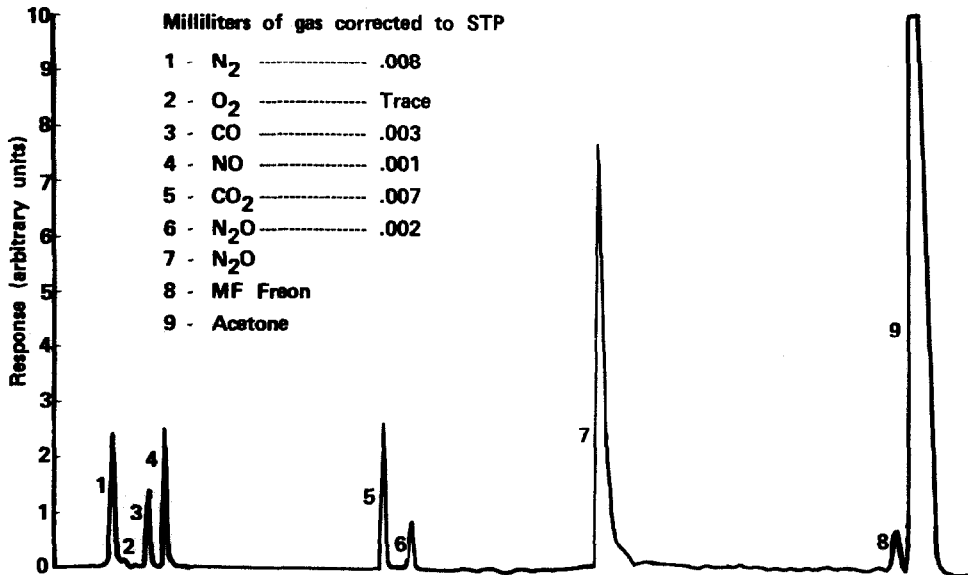7 - N_2O
8 - MF Freon
9 - Acetone

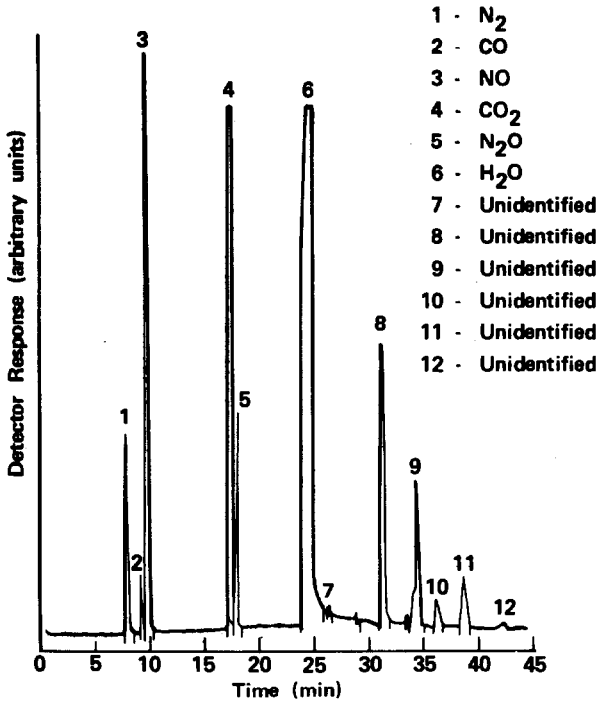Fig. 6.   Chemical Reactivity Chromatogram of LX-13

Fig. 7. Chemical Reactivity Test Chromatogram for a Typical Run on the Propellant AHH (Sample Conditioned at 100 C for 22 Hours)

vity. The acceptable degree of reactivity will depend on the application. If the materials are to be in contact for long periods of time then the ratio must be smaller, but larger ratios can be accepted if the contact time is shorter. If the ratio is very large then it may be unsafe for the material to be in contact with the explosive for short periods of time.

Table 1 gives data obtained for LX-13 and two mold releases. These data show the Price Discroll to be reactive and the zinc stearate to be nonreactive. From

TABLE 1

Chemical Reactivity Test Results for LX-13 with Two Mold Releases (mℓ of Gas Corrected to STP)

	N_2	CO	NO	CO_2	N_2O	Total
LX-13	0.012	–	–	0.002	–	0.014
Price Discroll	0.015	–	–	0.003	–	0.018
LX-13 + Price Discroll	0.042	–	0.016	0.040	0.088	0.186
Zinc Stearate	0.009	–	–	0.006	–	0.015
LX-13 + Zinc Stearate	0.015	–	–	0.005	0.001	0.021

these data, it was recommended that the zinc stearate be used rather than the Price Discroll.

PBX 9404 was tested with Epon 828 cured with different curing components and data are given in Table 2. These data show that the component used to cure the Epon 828 affects the reactivity with PBX 9404 and that Ajicure C003 is less reactive than the other curing agents. However, in both cases there was an increase in nitrous oxide and nitrogen and a decrease in nitric oxide and carbon monoxide in the mixtures.

The data obtained with PBX 9404 and CPR 1009-7B gave some unexpected results. The total volume of gas for the mixture was less than the sum of the components and there was no nitric oxide in the mixture. This indicated that CPR-1009 acts as a stabilizer for the nitrocellulose in the PBX 9404. This was also supported by the blue color of the PBX 9404 after the test. Normally, the PBX 9404 turns a light brown due to the nitration of its stabilizer diphenylamine.

Table 3 gives CRT results of extremely reactive materials. RX-08 is an experimental explosive developed by LLL and alone it is thermally stable, but with Epon 828 it is very reactive.

The CRT apparatus has been used to investigate the thermal decomposition of PETN and the propellant AHH.

An investigation was planned to study the low temperature decomposition of PETN using the CRT system, but some preliminary runs on various lots of PETN gave completely different results. These differences were investigated and it

TABLE 2

CRT for PBX 9404 with Epoxies (ml of Gas Corrected to STP)

	N_2	CO	NO	CO_2	N_2O	Total
PBX 9404	0.025	0.043	0.197	0.122	0.021	0.408
	0.023	0.038	0.205	0.116	0.020	0.402
Epon 828/	0.010	–	–	0.025	–	0.034
Ajicure LX-1	0.005	–	–	0.025	–	0.027
PBX 9404 + Epon 828/	0.268	0.004	0.034	0.120	0.962	1.390
Ajicure LX-1	0.276	0.004	0.052	0.136	1.074	1.540
Epon 828/	0.011	–	–	0.014	–	0.025
Ajicure C003	0.012	–	–	0.010	–	0.022
PBX 9404 + Epon 828/	0.110	0.004	0.010	0.072	0.268	0.470
Ajicure C002	0.102	0.004	0.008	0.070	0.276	0.462
CPR 1009-7B	0.084	–	–	0.053	–	0.137
PBX 9404 + CPR	0.118	0.004	–	0.102	0.018	0.242
1009-7B	0.142	0.006	–	0.118	0.018	0.282

TABLE 3

Chemical reactivity Test Data for RX-08 with Epon 828 (ml of Gas Corrected to STP)

	N$_2$	CO	NO	CO$_2$	N$_2$O	Total
RX-08	0.030	0.001	0.001	0.015	0.002	0.067
Epon 828	0.007	0.008	-	0.001	-	0.015
RX-08/Epon 828	1.016	0.398	0.525	2.263	1.814	6.015

was determined that the thermal decomposition rate of PETN is particle size-dependent as can be seen in Fig. 8.

To identify some of the additional peaks, the CRT system was interfaced to a Bendix Model 14-107 time-to-flight mass spectrometer. From CRT/MS runs on different lots of PETN four different compounds were detected and identified. These are given in Table 4.

The thermal decomposition rates were determined for the double base propellant AHH[+] using the CRT system. Fig. 9 is a plot of the gas evolved per gram of sample
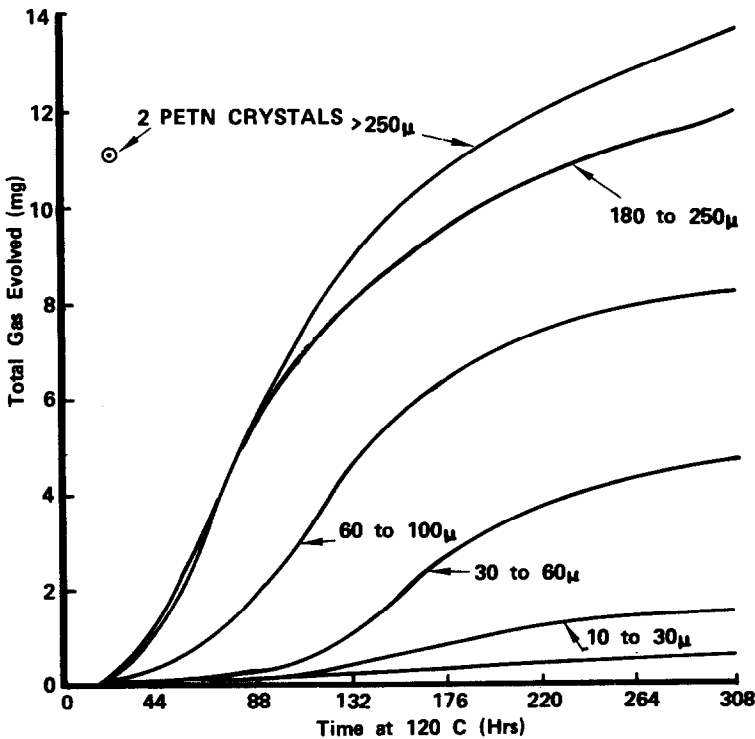

Fig. 8. Total Gas Evolved from PETN Samples of Different Particle Sizes

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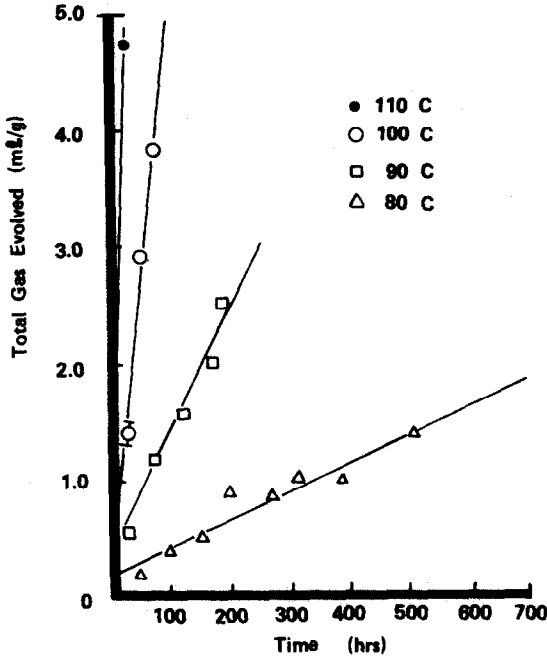[+]L. C. Myers, Thermal Decomposition of a Double-Based Propellant AHH - Part II, MHSMP-77-59, October 1977.

Fig. 9. Total Gas Evolved per gram of AHH Propellant as a Function of Time at Different Temperatures
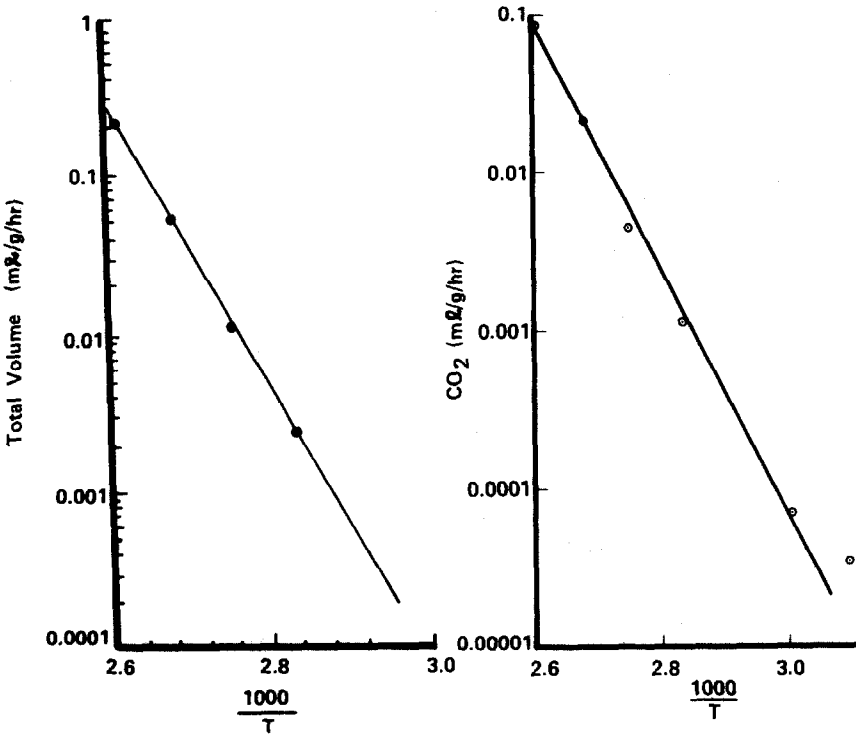
TABLE 4

Compound Identified in CRT From PETN

Cyanogen	Decomposition Product
Hydrogen Cyanide	Decomposition Product
Carboyl Sulfide	From a Sulfur Impurity Introduced During
Carbon Disulfide	Synthesis

as a function of time at different temperatures. The log of the total volume of gas and the log of CO_2 evolved were plotted as a function of the reciprocal of the absolute temperature as shown in Fig. 10.

For CO_2 the 110 C to 60 C data are linear, but there is a change in the kinetics at 50 C.

Fig. 10. Arrhenius Plots of Total Gas Volume and CO_2 Evolved from AHH Propellant