27

11/3/80 S.

NTIS

240

SAND80-1862/1
Unlimited Release
UC-45

The Deflagration-to-Detonation Transition Project: Quarterly Report for the Period December 1979 Through February 1980

MASTER

Morton L. Lieberman, Editor

Prepared by Sandia National Laboratories, Albuquerque, New Mexico 87185
and Livermore, California 94550 for the United States Department
of Energy under Contract DE-AC04-76DP00789

Printed September 1980

Sandia National Laboratories

SF 2900-Q(3-80)

Issued by Sandia Laboratories, operated for the United States Department of Energy by Sandia Corporation.

SF 1004-DF(11-77)

Printed in the United States of America

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Printed Copy ; Microfiche $3.00

PAGES 1 to 2

WERE INTENTIONALLY

LEFT BLANK

SAND80-1362/1 UC-45

Unlimited Release

Printed September 1980

THE DEFLAGRATION-TO-DETONATION TRANSITION PROJECT: QUARTERLY REPORT FOR THE PERIOD DECEMBER 1979 THROUGH FEBRUARY 1980

M. L. Lieberman, Editor
Initiating and Pyrotechnic Components Division 2515
Sandia National Laboratories
Albuquerque, NM 87185

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ACKNOWLEDGEMENTS

Numerous individuals contributed to both the writing and technical content of this report. Authorship is indicated by names in parenthesis following section titles. Task leaders and technical contributors are identified at the beginning of Sections II - V.

SUMMARY OF REPORT

Development of the MC3533 detonator is underway. An ignition sensitivity study has resulted in the selection of a 0.0016 inch diameter Tophet A bridgewire. A component design matrix has been defined and a purchase requisition has been placed for MRS requirements. Shock testing of CP via air gun tests has shown that the confined powder can withstand shock pulses averaging 13,600 g over a 0.9 ms period without igniting or experiencing any apparent degradation. A matrix of tests to assess density-length tradeoffs in the ignition, DDT, and output regions of a detonator is in progress; results obtained from the first twenty-two detonators established a suitable set of boundary conditions. Output of the MC3423 has been significantly increased by filling the cavities beyond the output charges with XTX-8003. Mixtures of B/$CaCrO_4$/CP were rejected for use in the MC3196A delay detonator primarily because of unsatisfactory scatter in function time. The design selected utilizes a 5.0 ± 0.5 mg pad of B/$CaCrO_4$ against the bridgewire followed by CP. This design was chosen after function time was determined as a function of B/$CaCrO_4$ mass and after it was shown that the selected conditions did not introduce an RAF problem.

Compatibility results obtained from mini-dets after 1078 days show that no measurable instability (Co^{+2} formation) in CP occurs at or below 80°C; also, the observed reaction at 120°C appears to have equilibrated, since Co^{+2} values for 612, 795

and 1078 day samplings are comparable. Thermo-mechanical analysis performed with CP loaded in MC3196 charge holders has established that no thermal incompatibility, i.e., pellet slippage, occurs during repeated thermal cycling over the range -50 to 125°C. Activation energies determined for thermal decomposition of CP and B/$CaCrO_4$/CP suggest that no thermal interactions occur between CP and B/$CaCrO_4$. Both DSC and TGA measurements of CP decomposition under flowing ammonia support the hypothesis that this gas suppresses reaction.

Three new lots of CP have been synthesized and some materials characterization has been performed. All-fire performance testing of two of the lots have established that they yield acceptable results for the MC3423 detonator. Additional work to establish the initial thermal decomposition products of CP has commenced. This work includes development of separation methods for the various compounds, as well as analytical chemical studies. Preliminary work on a high pressure liquid chromatographic method for the determination of as little as 1% amide in CP appears encouraging. Studies on chemical analogs of CP are continuing. Efforts are being made to develop natural abundance N-15 NMR spectra of CP and its analogs. Single crystal x-ray diffraction analyses have established that the two compounds analyzed both exhibit cobalt bonding to the tetrazole ring in the N-2 position. Surface areas of the analogs have been measured.

Experimental studies for the determination of equation-of-state properties of both unreacted CP and its reaction products have been performed and the data are being analyzed. The effect of powder density ρ on detonation velocity D^* is given by the equation

$$D^* = 0.868 + 3.608\,\rho\ ,$$

where density is in Mg/m^3 and velocity is in km/s. Optical studies of DDT have shown that an initial period of low velocity (0.2 km/s) burn occurs which can be short-lived. This has been shown to transition to a mode believed to be low velocity (1 km/s) detonation. The latter then transitions to full detonation after a run distance which is dependent on the initial CP density. Modeling of DDT has continued with recent efforts focusing on code development.

CONTENTS

THE DEFLAGRATION-TO-DETONATION TRANSITION PROJECT: QUARTERLY REPORT FOR THE PERIOD DECEMBER 1979 - FEBRUARY 1980

I. INTRODUCTION (M. L. Lieberman)

The Sandia National Laboratories project on deflagration-to-detonation transition (DDT) has been underway since September 1978. Major support is being provided by Unidynamics/Phoenix, Inc. and Mound Facility, while a variety of other institutions are performing specialized tasks. The activities of this project pertain primarily to the development of small, safe, low-voltage, hot-wire detonators. Its major goals are (a) the formulation of a modeling capability for DDT of the explosive 2-(5-cyanotetrazolato)pentaamminecobalt(III) perchlorate (CP); (b) the development of improved DDT materials; (c) the establishment of a data base for corrosion, compatibility, and reliability of CP-loaded detonators; and (d) the design and development of advanced DDT components.

Because many people are involved in these activities, quarterly reports (1-5)* are being issued as a means of disseminating current preliminary information on a timely basis. The report for the first quarter provided an overview of the project activities, specific objectives, plans, and current data. Following reports have given additional data and results when obtained.

---

*All references are given in one section at the end of the document.

II. PHYSICS OF CP DDT

Task Leader - P. L. Stanton, 2513

Technical Contributors - R. J. Haushalter, 1556
E. A. Igel, 1556
F. M. Tamashiro, 1556
D. J. Mullikin, 2513
M. A. Rumsey, 2514
F. J. Salas, 2514
A. C. Schwarz, 2515
E. E. Jones, 4253
H. Krier, Combustion Sciences, Inc.
S. G. Gokhale, " " "
L. M. Lee, Ktech Corporation
G. T. West, Pantex
J. H. Mohler, Mound
J. W. Fronabarger, Unidynamics/Phoenix, Inc.

A. Overview (P. L. Stanton)

The experimental studies for the determination of equation-of-state properties for both unreacted CP and the reaction products have been completed. The data are now being analyzed, and some of the detonation properties can now be specified. A discussion of the nature of CP as an explosive is presented in the next subsection.

Direct optical observation of DDT in a CP column has been accomplished. An experiment configuration has been developed in which it is expected that the effects of variables such as loading density, particle size, etc. on run distance to detonate can be observed.

Progress in modeling and experimental studies was discussed in a DDT Physics review meeting held at Sandia on February 14. Much of the progress presented then is documented in this report.

B. Observations on the Nature of CP as an Explosive (P.L.Stanton)

Data on CP have been obtained in a variety of experiments directed toward measurement of specific properties. These experiments have provided additional information which encompasses various forms of knowledge from empirical characterization to an intuitive feel for the nature of CP relative to other explosives. In this section, some of these observations are set forth.

The first characteristic of CP that should be noted is its compaction behavior. Relatively high pressing pressure is required to consolidate CP and the frictional forces developed in a pressing die are relatively great (see Reference 6, SAND79-1833, The Compaction Behavior of Ten Pyrotechnic Materials, by O. L. Burchett, et al). This results in limitations on the range of densities achievable in a test device or in a component. Thus, any CP device will have appreciable porosity and will resist compaction due to dynamic loading as well. Densities obtainable range from the bulk density, about 0.88 to about 1.8 Mg/m^3.

The burning characteristics of CP indicated in the various DDT experiments are that low velocity (0.2 km/s) burn can be achieved. Often it is short-lived and rapidly transitions to a mode believed to be a low velocity detonation (LVD). The LVD propagation rate is about 1 km/s. The LVD transitions to full detonation after a run distance which depends on the initial density. The run distance appears to increase sharply with increasing initial density. Run distances as low as 3 mm have been observed at a density of 1.3 Mg/m^3. Initiation of this burn-LVD mode is readily accomplished with a hot wire or low energy EBW.

In full detonation, the detonation pressure and propagation velocity are comparable with other intermediate high explosives. As with other explosives, the pressure and velocity increase with increasing initial density. Detonation pressure at maximum theoretical density (TMD) should be well over 30 GPa and detonation velocity over 7 km/s.

From the cylinder expansion tests performed at Pantex, it appears that CP has greater <u>brisance</u> than would be predicted from the detonation pressure estimates. The CP-loaded cylinder produced greater damage in the mounting plate than did PBX 9404, although the CP loading density was only 1.6 Mg/m^3 or less.

The Gurney energy is estimated from these cylinder expansion tests to be 2.7 MJ/kg for a density of 1.66 Mg/m^3. This places CP below average in ability to accelerate metal.

The impact sensitivity of CP is much greater than that of other secondary explosives. In initial slapper testing, with the slapper devices presently available, it was impossible to produce sufficiently low velocities to obtain a short-pulse threshold. Gun impacts resulted in long-pulse threshold data points comparable to those for low density PETN.

C. DDT Modeling (P. L. Stanton)

The DDT modeling effort is continuing at Combustion Sciences, Inc. (CSI), under the direction of Dr. Herman Krier.

In the first stage of the current study, one-dimensional, two-phase flow equations were developed for a mobile bed of granular propellants by using the Lagrangian formulation. These equations, in general, are different from the Eulerian formulation with respect to convective derivative terms. Almost all other details of the Eulerian formulation, namely, momentum and heat transfer, inertial and energy coupling terms, and mass source terms arising from the reactive nature of the problem, were retained in this new formulation. Two sets of equations were developed - one for the mixture and the other for the gas phase. With appropriate coordinate transformation, these governing equations for both phases were reduced to single space and time variables. This was necessary if one desired to utilize the logic in the Sandia Laboratories WONDY hydro-code. Particle phase variables were subsequently obtained from algebraic identities defining homogeneous mixture variables (density, velocity and energy). These equations were found to be significantly different from the existing equations in the WONDY code.

In the next stage, a numerical code has been developed by using a centered second order finite difference analog. However, the presence of

1) interaction and transfer terms,
2) nonlinear source terms, and
3) spatial gradients in all the governing equations,

made it almost impossible to utilize the existing WONDY code for current two-phase DDT flow computations.

During the last four months a code was developed with logic similar to the existing Eulerian approach. That means, based on known variables at time <u>n</u>, finite increments of all the flow variables at <u>n</u> were obtained and then variables at new time, <u>n+1</u>, were computed. The initial conditions as well as the boundary conditions were for flow causing DDT in closed pipe studies. As opposed to WONDY, this code is not an evolving code (newly computed values used only in the next integration cycle). For the trial cases, a severe instability was building in few integrations. Smaller values of the grid size or the time step did not help in preventing this instability.

This approach has therefore been discontinued for the time being. CSI is currently developing a code which uses an integration logic which is now very similar to that of the WONDY code. The major stumbling block in such a logic is obtaining the values of all the flow variables at all the half and full grid spacings. Another problem is in calculating the velocities at the required instant of time needed in the calculations. For example, velocities which are obtained by integrating momentum equations are at half time step <u>$n + \frac{1}{2}$</u>. But for evaluating the source, transfer and interaction terms, one needs the velocity values at time <u>$n + 1$</u>. CSI is investigating the importance of these and similar approximations.

Depending on the successful outcome of this new code in the next several months, CSI would then investigate the following physics for the DDT flow mechanisms:

(1) the stress work term - its form and significance in DDT studies.

(2) cemented bed concept or flow through immobile bed.

(3) effect of interaction momentum and heat-transfer terms.

(4) effect of grid size, stability criteria and artificial viscosity to the calculations of detonation (shock) information.

(5) rezoning features (as with the existing WONDY code).

(6) generalizing boundary and initial conditions.

(7) comparing predictions of DDT run-up length to data now being obtained for the CP porous bed from tests currently being carried out at Sandia Laboratories.

D. Cylinder Expansion Tests (P. L. Stanton)

The cylinder expansion test series at Pantex (under the direction of George West) has been completed and the data are being analyzed. Some preliminary results are available and are discussed here.

The cylinder expansion test device consists of a stick of explosive in a copper sleeve. The explosive is detonated from one end and as the detonation sweeps down the stick, the sleeve expands radically due to the pressure in the detonation products. The wall velocity as a function of time is obtained from streak camera records.

This test series consisted of "quarter-scale" cylinder expansion tests on the explosives CP, ABH, and PBX 9404. For safety and economy, the standard explosive cylinder (1 inch diameter, 12 inch long) was scaled down by one quarter. The copper sleeve wall thickness was scaled down from 0.120 inch to 0.030 inch. To verify scaling, the first tests were done with PBX 9404, for which a good data base exists.

An important observation regarding these experiments was the effect of the incremental loading of the cylinders. The ABH and CP devices were loaded by consolidating the bulk powder directly into the sleeves. The increments were chosen to produce l/d ratios of 1.0. In the experiments, a high-speed framing camera was used to monitor the overall device behavior. The framing camera showed an obvious variation in reflectivity of the cylinder periodically along its length, with periods corresponding to the pressing increment length. This is interpreted as variations in the cylinder wall motion due to corresponding variations in the pressure and/or detonation velocity in the explosive with local density. At the very least, this confounds the data analysis. Further tests are planned using cylinders loaded in much finer increments.

The results presently available from these tests are summarized in Table II.D.1. The indicated velocity of detonation variation D^* with density ρ is

$$D^* = 0.868 + 3.608\ \rho\ ,$$

where density is in Mg/m^3 and velocity is in km/s.

TABLE II.D.1 Preliminary

Data from Pantex Cylinder Expansion

Tests with CP

Loading Density, Mg/m^3	Detonation Velocity,* km/s	Wall Expansion Velocity at 4.5 mm,** km/s
1.12	4.895 ± 0.035	1.01
1.38	5.888 ± 0.012	1.18
1.39	5.870 ± 0.014	-
1.66	6.844 ± 0.080	1.36

* ± Values are standard deviations from four probe pairs on each shot.

** Average velocity of left and right side after 4.5mm expansion.

E. Detonation Pressure Measurements in CP (P. L. Stanton)

This test series, described in detail in the previous quarterly report(5), is now essentially completed. The results are only slightly different from the preliminary values given in that report. The data are being analyzed for further information content.

F. Optical Studies of CP-Loaded Devices (E. A. Igel)

Eight experimental devices, each containing approximately 15 mg of CP (UMC Lot No. 47344), were assembled in the clear header configuration shown in Figure II.F.1. The CP was pressed against the sapphire substrate at targeted densities of 1.42 and 1.62 Mg/m^3 to form a cylindrical pellet, 5 mm diameter by 0.50 mm long. The open face of the pellet was confined by pressing a lanthanum-modified lead zirconate-titanate (PLZT) powder (crystal density of 7.8 Mg/m^3) against the CP with the same force used in constructing the CP pellet. In all experiments the slit of the recording streak camera was aligned at the midpoint of, and perpendicular to, the bridgewire, as is also shown in Figure II.F.1. Devices were ignited by applying a constant current pulse of approximately 65 amperes to the one ohm bridgewire.

All recordings show an initial radiant emittance starting at the bridgewire and then moving away from it at a relatively low velocity. Within one to three microseconds this burn rapidly accelerates to a constant deflagration velocity over the remaining 2mm explosive path provided by this experiment.

FIGURE II.F.1

CLEAR HEADER CONFIGURATION

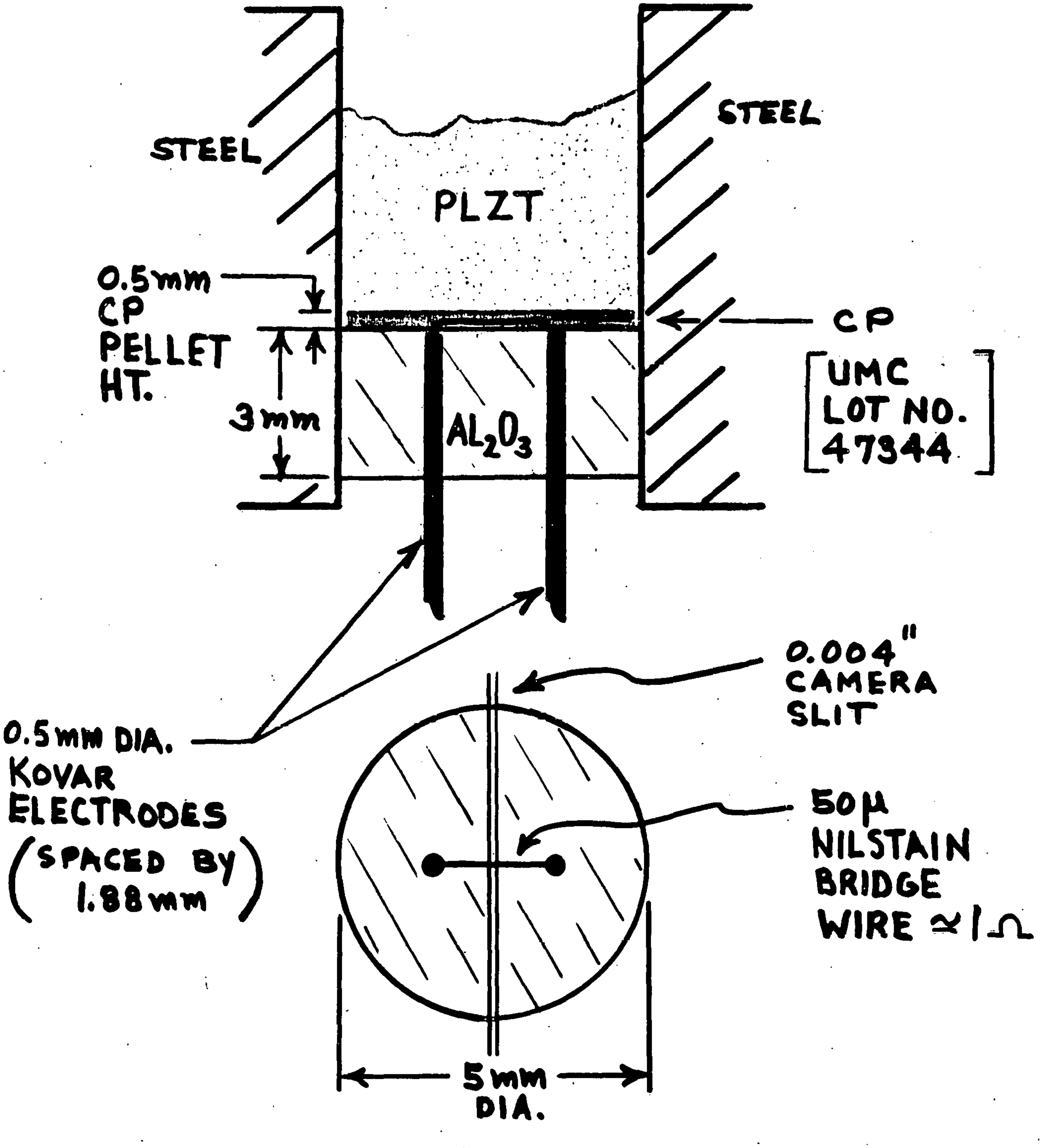


Figure II.F.2 shows a reasonably typical displacement versus time function for an interfacial reaction at two different densities. The rate of initial burn is clearly responsive to the density of CP surrounding the bridgewire and values of 61 and 259 m/s are found for CP densities of 1.42 and 1.62 Mg/m^3, respectively. As the burn grows radically and reaches an approximate distance from the bridgewire of 0.5 mm, a transition is made to a deflagration velocity of 760 and 790 m/s for CP densities of 1.42 and 1.62 Mg/m^3, respectively. The noted velocity difference is not statistically significant because our limited number of samples describe a non-Gaussian distribution. Results given in Table II.F.1 are arranged in order of ascending density and the double entry values for initial and deflagration velocities show the velocity difference, if any, for the reaction as it expands from both sides of the bridgewire-ignition-area.

TABLE II.F.1 CP Deflagration Velocities

Shot No.	Density Mg/m^3	Initial Velocity m/s		Deflagration Velocity m/s	
1	1.42	61	61	767	754
2	1.43	35	35	1036	854
7	1.43	35	35	727	727
5	1.46	96	96	839	733
6	1.59	79	79	824	577
8	1.59	248	248	613	788
3	1.62	259	259	795	795
4	1.63	306	306	810	810

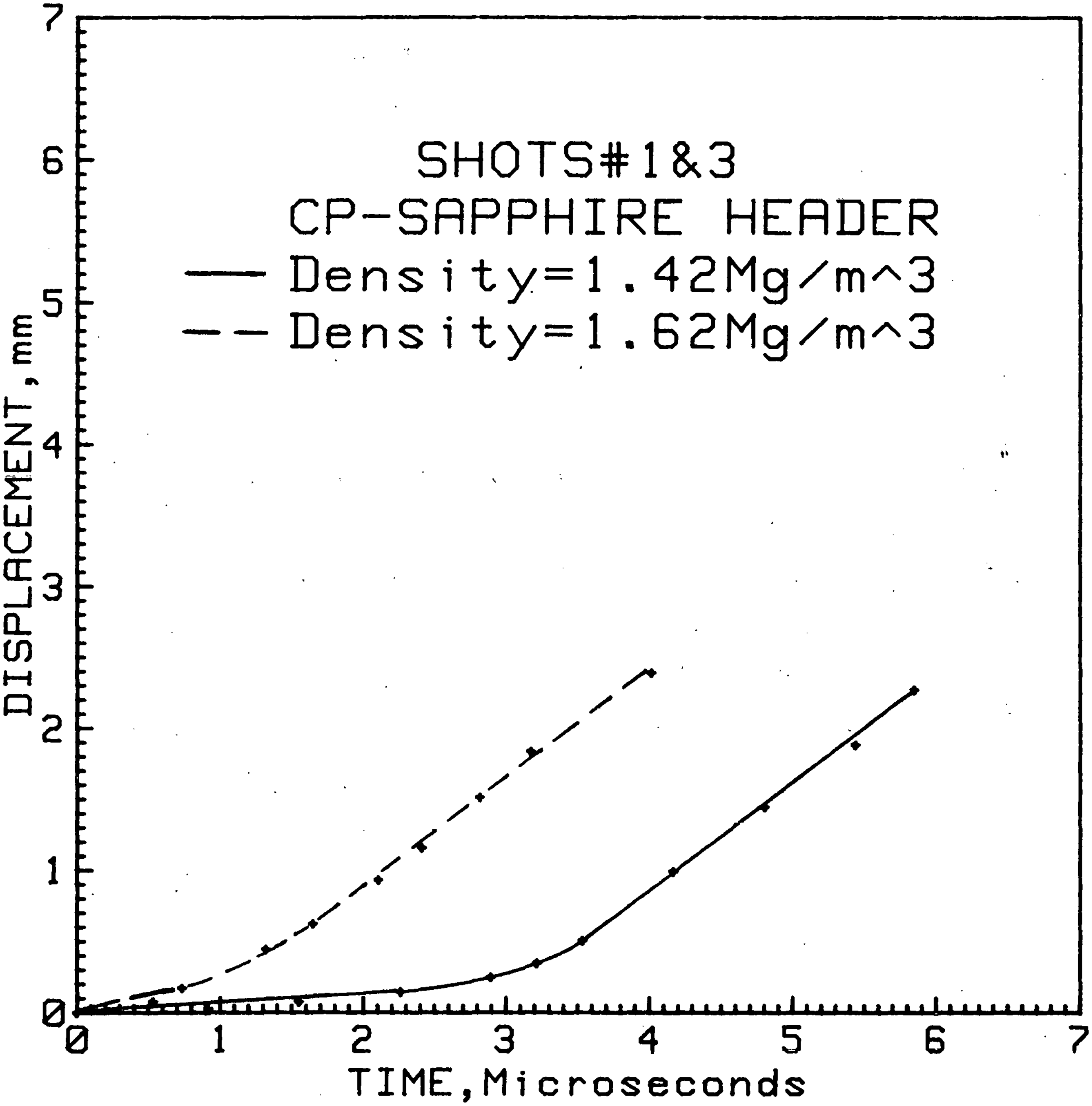


FIGURE II.F.2

DISPLACEMENT VERSUS TIME FOR CP DEFLAGRATION

Additional information that may be of some interest is listed in Table II.F.2.

TABLE II.F.2. Data for Deflagration Rate Experiments

CP Density, Mg/m^3	$1.42 \pm .02$	$1.62 \pm .02$
Function Time, μs	13 ± 1	10 ± 1
Total Energy Delivered to Bridgewire, mJ	59 ± 6	47 ± 5

During the next report period we hope to experimentally demonstrate that the interfacial burn phenomenon is not a function of CP pellet lengths greater than 0.5 mm; if confirmation is obtained, additional experiments, identical to those described, will be conducted at CP densities of 1.30 and 1.75 Mg/m^3. Experiments in which ignition is provided by smaller firing currents, e.g. less than 15A, would also be of interest. However, the attendant jitter in function time at these relatively low firing currents might not be compatible with our temporally limited but high resolution photographic recording interval.

G. Optical DDT Studies With CP-Loaded Capillary Tubes (E.A.Igel)

Pyrex capillary tubes having an outside diameter of 6 mm and an inside diameter of 1.1 mm were loaded with CP to provide a total explosive column length of approximately 16 mm. The 1.1 mm diameter column was incrementally loaded using a length to diameter ratio of one and the targeted density was 1.42 Mg/m^3.

An SE-1 header was cemented to one end of the pyrex tube and ignition was obtained only by using a CDU (1 μf @ 1.5 KV) because the arrangement allowed venting at the ignition area. The slit of the streak camera viewed a 0.1 mm wide linear explosive area which was parallel to the column's longitudinal axis. Preliminary results from four shots are listed in Table II.G.1.

TABLE II.G.1 DDT Data for CP in Capillary Tubes

Density Mg/m^3	Deflagration Velocity m/s	Distance to DDT mm	Detonation Velocity m/s
1.42	800	12.5	3460
1.51	931	None	----
1.51	944	None	----
1.53	1278	*	----

*Deflagration died after 12 mm of travel.

For the two cases in which the deflagration proceeded to the end of the explosive column at velocities of 931 and 944 m/s, the luminosity of reaction was not contiguous.

A much improved experimental arrangement, designed by Stanton (2513) and Mullikin (2513), comprised counterboring the capillary tubes to accommodate a diameter-modified SAD-1031 header. With this arrangement we were able to hot wire ignite the explosive column with a 80 ampere pulse which in turn minimized stray light from interfering with and/or masking the velocity record. Results are given in Table II.G.2.

TABLE II.G.2 CP DDT Data for
Hot Wire Ignition of Capillary Tubes

Tube Material	O.D. mm	I.D. mm	CP Density Mg/m^3	Deflagration Velocity m/s	Distance to DDT mm	Detonation Velocity m/s
Pyrex	8	2.0	1.31	973	2.7	5216
Pyrex	8	2.0	1.31	1555	3.5	4725
Quartz	8	1.7	1.36	1022	11.2	5017

For those cases in which the DDT length is only a few millimeters, the photographically recorded deflagration velocity is a convolution of true deflagration velocity and propagation geometry, i.e. Huygenian wave geometry. Thus measurements of deflagration velocity must be deconvolved. Our preliminary analysis does not give a deconvolved value but instead an average or psuedo deflagration velocity. A contributing complication to the deflagration process is that the optical confining material, glasses, will support fracture propagation at rates higher than those from deflagration. All recordings, although few in number, show an unexplained marked decrease in radiant emittance for a distance of one to two millimeters prior to DDT, as if there was an endothermic reaction or possibly a phase change which optically precludes ionization or optically decouples most of the deflagration-radiation away from the observational direction. When detonation does occur, it may occur at the center of the explosive column and then propagate backwards to the periphery of the column. Photographic complications arise in trying to detail this transition zone because the radiant emission from detonation is 400 to 1000 times greater than that from deflagration. Once detonation commences and proceeds down the column there is no problem in recording and measuring a reliable velocity. Much interesting work remains to be done.

III. MATERIALS DEVELOPMENT

Task Leader - M. L. Lieberman, 2515

Technical Contributors: D. L. Marchi, 2515
V. M. Loyola, 2516
T. M. Massis, 2516
J. E. Womelsduff, 2516
B. Morosin, 5154
E. J. Graeber, 5822
K. Bullock, Mound
W. Collins, Mound
D. M. Colman, Mound
G. Jendrek, Mound
D. M. Kapsch, Mound
C. Kinard, Mound
E. M. Pitre, Mound
J. W. Reed, Mound
D. Sullenger, Mound
W. Fleming, Unidynamics
J. Fronabarger, Unidynamics
E. A. Deutsch, U. Cincinnati

A. Overview (M. L. Lieberman)

Studies have continued to further understand the material properties and behavior of CP, to improve methods of its analysis, and to develop improved explosive materials. Work on chemical analogs of CP have provided a basis for chemical "tailoring" of explosive properties.

B. NMR Analysis of CP Analogs (V. M. Loyola)

The carbon-13 and proton NMR studies which have been carried out on the CP analogs have been described previously (4,5). That work established that the analogs are indeed pentaammine cobalt (III) complexes of the appropriate tri- or tetrazole compounds. At that time it was indicated that additional NMR work, i.e. natural abundance nitrogen-15, was being contemplated at Colorado State University in order to allow unambiguous assignment of the correct bonding between the heterocyclic ligand and the pentaammine cobalt (III) portion of the molecule. This work has been delayed due to the requirement for a safe operating procedure and also slow in developing due to some technical difficulties encountered with both the instrumentation and the chemistry involved with the natural abundance nitrogen-15 NMR experiment.

Some progress has been made toward the solution of both problems. The safety concerns appear to have been satisfactorily addressed by the submission by M. L. Lieberman (2515) to B. Hawkins (CSU), of an extensive collection of safety information and documentation of prior experimentation which has been carried out on CP. The collection of information was composed of contributions from Sandia, Unidynamics, Mound and SRI. The technical aspects have been both instrumental and chemical, the former having been addressed solely by CSU since they are responsible for the upkeep of their instruments; the latter have been addressed by both CSU and Sandia personnel. Some work carried out on some selected tetrazole compounds indicates that natural abundance nitrogen-15 NMR is possible with the special NMR technique of gated decoupling. Similar work is continuing on the bromide salt of the CP amidine chelate complex, a non-explosive salt, in order to establish the experimental conditions necessary to collect data from the complexes themselves, however, no information is currently available to either confirm or deny the feasibility of this work.

C. Crystal Structures of CP Analogs (B. Morosin)

Part of the Deflagration-to-Detonation Transition Project in Dept. 2510 has involved the preparation and materials properties study of a variety of new materials chemically similar to 2-(5-cyanotetrazolato)pentaammine cobalt(III) perchlorate, CP. The electron withdrawing characteristics of various substituents of the five member (N and C) ring of the ligand, such as the 5-cyano-group, alter the bonding capabilities and hence the nature of these energetic perchlorate compounds. Two such substitutions for the 5-cyano-group which should alter the nature of the chemical bonding in the complex are the 5-methyl- and the 5-(3,5-dinitrophenyl)-groups. Crystal structure studies have been initiated on these materials, both of which prove difficult to crystallize in usable, untwinned forms. The 5-methyl analog crystallizes in $P2_1/a$ with a = 16.043, b = 7.577, c = 12.391 Å and β = 97.32° with four molecules per cell. Preliminary results on 2630 hkℓ observations show that the tetrazole ring is bonded in the 2-position, similar to CP. Only unit cell data has been deduced on the 3,5-dinitrophenyl analog because of the poor quality of crystals to date. This material is orthorhombic with a = 14.044, b = 35.876 and c = 8.516 Å. Recrystallization under slightly different conditions is being attempted to prepare the desired size specimen necessary for more detailed studies.

D. Surface Area Measurements of CP Analogs (T. M. Massis)

BET surface area measurements on candidate DDT materials were performed using the Micromeritics 2500 Digisorb surface area analyzer. All samples were run in duplicate using a five point method with krypton or nitrogen as the adsorbing gas. Table III.D.1 lists the samples and the respective surface area data. For comparison the SLA, Mound and Unidynamics values for the CP sample were similar.

Additional data are weight loss measurements for each sample. These weight losses are due to volatile materials such as water on the surface when processed for surface area measurements. Weight loss data are based upon the actual weight of the sample placed in the surface area tube compared to that after degassing at 100-110° C for 24 hours (minimum) and a vacuum of 1 micron or less.

TABLE III.D.1

Surface Area Measurements

	NAME	ACRONYM		Surface Area (m^2/g)		Weight Loss (%)
				KRYPTON	NITROGEN	
1.	2-(5-Cyanotetrazolato) pentaammine-cobalt(III) perchlorate	CP	A.	0.65		0.17
			B.	0.68		0.30
2.	2-Tetrazolatopentaamine-cobalt(III) perchlorate	TzHPCP	A.	1.32		0.35
			B.	1.32		0.26
3.	2-(5-Chlorotetrazolato) pentaamine-cobalt(III) perchlorate	5ClTzPCP	A.	0.18		0.50
			B.	0.18		0.44
4.	2-(5-Nitrotetrazolato) pentaammine-cobalt(III) perchlorate	$5NO_2TzPCP$	A.	0.74		0.77
			B.	0.73		0.54
5.	2-(5-Methyltetrazolato) pentaammine-cobalt(III) perchlorate	CH_3TzPCP	A.	0.52		0.33
			B.	0.53		0.93
6.	2-(5-Trifluoromethyl-tetrazolato) pentaamminecobalt(III) perchlorate	F_3TzPCP	A.	0.62		3.3
			B.	0.61		3.8
7.	Isothiocyanatopentaamminecobalt(III) perchlorate (COARSE)	ICCP	A.	0.46		0.70
			B.	0.46		0.71
8.	Isothiocyanatopentaamminecobalt(III) perchlorate (FINE)	ICCP	A.	1.02		<0.01
			B.	1.02		<0.01
9.	Catena-u-cyanotetraamminecobalt(III) perchlorate	CATCP	A.	8.17	8.90	0.93
			B.	No Value	8.86	0.96
10.	1-(3-Nitro-1,2,4-triazolato)-pentaamminecobalt(III) perchlorate	$3NO_2$-S-TRPCP	A.	3.36		1.07
			B.	3.39		0.97
11.	1-(4-Nitro-1,2,3-triazolato)-pentaammine-cobalt(III) perchlorate	$4NO_2$-V-TRPCP	A.	0.36		4.8
			B.	0.36		4.4
12.	2-(5-(3,5-Dinitrophenyl-tetrazolato)pentaammine-cobalt(III) perchlorate	3,5DN-PhT_zPCP	A.	2.10		3.2
			B.	2.06		3.2

E. New Lots of CP (M. L. Lieberman)

Three additional lots of CP have been synthesized. Two are intended for use in the MC3423 detonator and the third is for development studies. The lots, in chronological order, are EL-58633, EL-58636, and EL-58641.

Lots EL-58633 and EL-58636 were both more difficult to sieve than earlier production lots with EL-58636 being the more difficult. Sufficient material passed through the sieves in each case to meet the lot acceptance criterion. Both lots appeared under low magnification optical microscopy to have agglomerated more than earlier ones. In the preparation of lot EL-58641 tighter controls were placed on several process parameters in the particle size adjustment recrystallization step. These included: (a) establishing the temperature of the isopropyl alcohol (IPA) container at $4.0 \pm 0.5^{\circ}$ C prior to the initial addition of the hot CP solution and (b) maintaining a temperature range of $31\text{-}35^{\circ}$ C in the IPA during subsequent CP solution additions. Lot EL-58641 sieved much better than did the prior two lots, although still not as well as lots EL-47345, EL-52211, or EL-47344.

X-ray diffraction analyses of the three new lots and the two prior production lots (EL-47345 and EL-52211) showed them to be identical and free of any distinguishing impurities. Scanning electron microscopy showed that lot EL-58641 was similar to early lots (EL-47345, EL-52211, EL-47344) in crystal size, extent of intergrowth, and absence of "amorphous" material.

Lots EL-58633 and EL-58636 appeared to exhibit increased extents of intergrowth and "amorphous" material.

Performance testing of ignition conditions was performed in MC3423 headers and is summarized in Table III.E.1. Data for the development lot EL-47344 are included for comparison. These results indicate that lots EL-58633 and EL-58641 provide satisfactory ignition behavior. Electrothermal response (ETR) data were obtained for igniters used in the performance testing of lots EL-58641 and EL-58633 before and after vacuum baking. Units of the former lot clearly showed no significant differences in gamma resulting from the vacuum baking. Units of the latter lot provided the same overall result, although there is reason to believe that some form of operator error and/or equipment malfunction yielded incorrect data for one group of units in the pre-baked condition. Because ETR is being used as an acceptance criterion in the MC3423 detonator program, considerable effort is being made to determine and rectify possible causes of such problems.

TABLE III.E.1

All-Fire Performance Testing of CP Lot

	EL-47344	EL-58641	EL-58633
Average all-fire current, amps	2.206	2.142	2.223
Standard deviation, amps	0.0387	0.0553	0.0337
99.9% low current, amps	2.003	1.842	2.050
99.9% high current, amps	2.408	2.436	2.400
Number of units	40	40	40

F. CP Decomposition Products (M. L. Lieberman)

This study is being performed by K. E. Bullock (Md), D. M. Colman (Md), and E. A. Deutsch (U.C.).

It was decided early in this quarter to make a coherent, logical attempt to determine the most likely decomposition products of CP based on known chemistry. This work was subdivided into two parts. First, develop a reasonable explanation for the conversion of CP into the amidine in DMSO solution; and second, look into the early steps of the low temperature thermal decomposition of CP. Numerous discussions and literature searches resulted in the postulated scheme outlined in Figure III.F.1 for the conversion of CP into amidine in solution.

The first step of this conversion involves loss of cyanogen from the tetrazole. The cyanogen remains in solution as does the resulting azido pentaamine cobalt (III) perchlorate. The cyanogen in solution is available to react with the azide yielding either 2-CP (starting material) or 1-CP. The 1-CP picks up water from the DMSO and is converted to the 1-amide.

Loss of water from this system could yield the amidine complex. Another possibility, however unlikely, is the loss of ammonia from the pentaamine in which case the carbonyl oxygen could act as the coordinating ligand.

It is interesting to consider the formation of the amidine during the actual production of CP in light of this scheme. The question of where is the 1-CP, that would be expected in some small percentage, has been raised numerous times. It seems

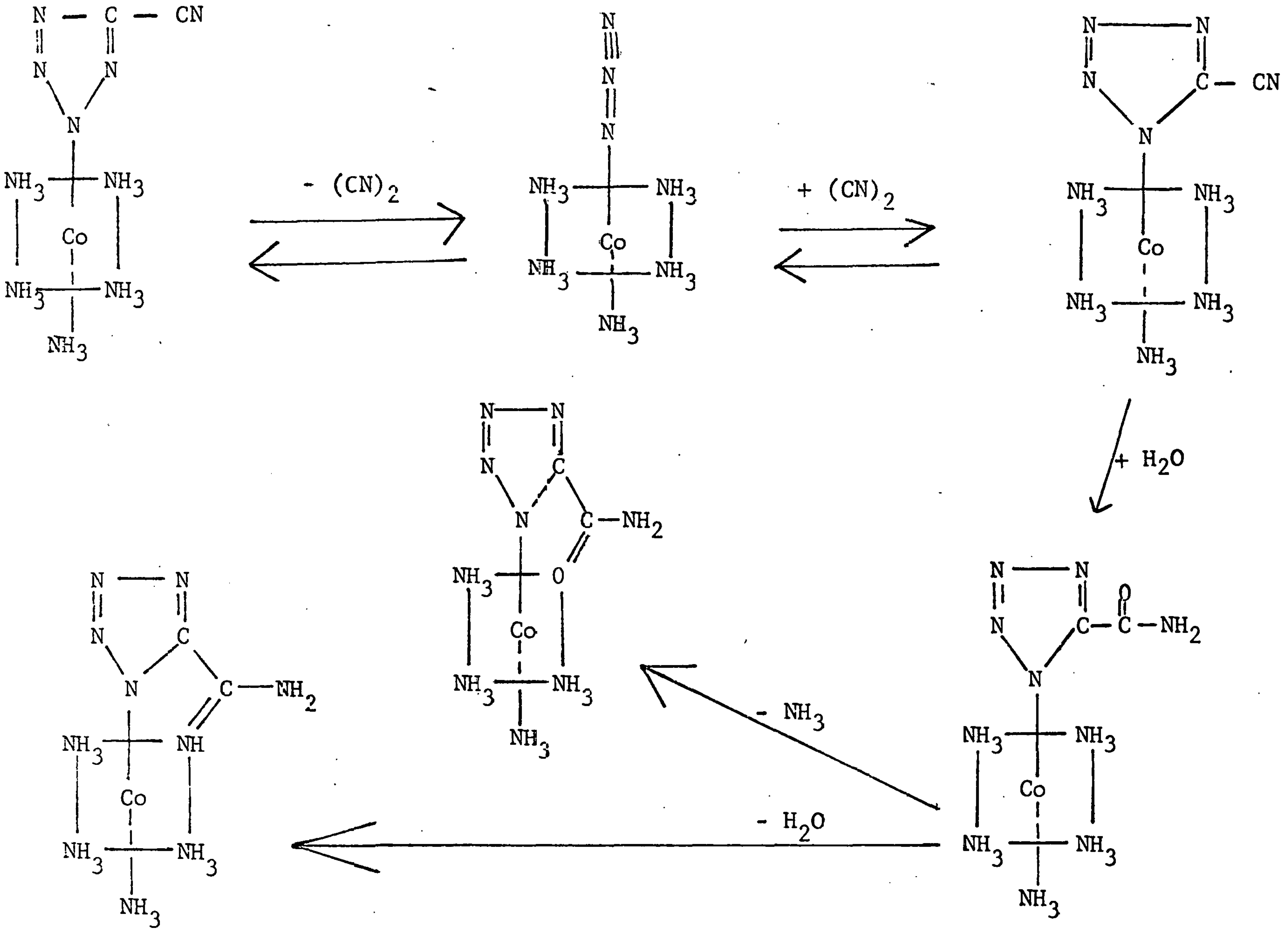


FIGURE III.F.1 POSTULATED REACTION SCHEME unlikely that only the 2 form is obtained; one would expect at least 1 - 5% of the 1-CP to be formed during the preparation of CP. It has also been noted that, in general, on tetrazoles, the substituents in the 5 position are more reactive if the tetrazole is also substituted in the one position as compared to those substituted in the two position. With the scheme presented in Figure III.F.1, it seems likely that any 1-CP formed is rapidly converted to amide and from there into amidine.

These assumptions are consistent with two facts: 1) no 1-CP has been isolated from CP preparation, and 2) amidine is formed in production. In addition the question is raised, is the amide impurity 1-amide, 2-amide or both?

Experiments have been designed to determine if the conversion scheme postulated in Figure III.F.1 is realistic or not. The primary experiment involved dissolving the azide complex in DMSO and bubbling cyanogen through the solution. As this was done the color changed from the deep purple of the azide to a yellowish-tan color. The solution was diluted with 0.1M $NaClO_4$ and fractionated on a Sephadex ion exchange column. Several fractions were collected. One of the fractions crystalized on standing. It was determined, by powder pattern, that these crystals are 2-CP. While this does not prove that the amidine is formed via this reaction, it does not disprove it and it does show that tetrazole rings can be formed in solution from azide and cyanogen. Attempts are being made to crystalize the remaining fractions for powder pattern determination as well as for other methods of analysis.

Simultaneous with this work, efforts were being made to understand the thermal decomposition of CP, particularly the early stages of decomposition. The primary interest was to determine which possible products should be analyzed for during compatibility studies. Once again, as in the solution work previously described, the tetrazole ring was believed to be the weakest portion of the molecule. The most likely mode of decomposition is loss of cyanogen. The cyanogen could react with adsorbed water in the CP to give hydrogen cyanide or it could remain as cyanogen.

Initially, during the determination of the melting point of the ligand, 5-cyanotetrazole, using the micro hot stage, it was noted that the compound undergoes decomposition prior to melting.

Decomposition was noted at 80° C when heated at a rate of 2°/min. As would be expected, the decomposition temperature varied with heating rate. The melting point of this compound was eventually determined on a gradient hot bench and was found in the range 98 - 102° C.

Spot tests, as described by Feigel in "Spot Tests in Organic Analysis", were used to determine that at least one of the decomposition products of 5-cyanotetrazole at 80° C is cyanogen. For these tests a small sample of the compound of interest is placed in the bottom of a vial which is then heated to the desired temperature. A small circle of filter paper impregnated with the spot test reagents is placed on top of the vial and is checked frequently to see if a positive reaction has occurred.

Since the cyanotetrazole appears to undergo decomposition at $\sim 80^\circ$ C, the test was repeated using CP (lot EL-47344). With heating to 140° C, NH_3 and cyanide were observed to be given off within 3 hours. Since it was felt that the cyanide could have come from cyanogen which had reacted with adsorbed H_2O in the CP, an experiment was set up in which the CP was mixed with P_2O_5 to trap any water. This sample was heated to $\sim 80^\circ$ C and cyanogen was detected. It was found that the cyanide test gives a positive reaction in the presence of cyanogen; and since this test is more sensitive than the cyanogen test, the experiment was repeated using the CP without P_2O_5, heating to $\sim 80^\circ$ C and testing for $CN^-/(CN)_2$ with the cyanide test. A positive reaction was obtained within 24 hours. No NH_3 was detected.

Based on these qualitative results, some thought should be given to the conditions used in drying the CP, since it appears that the first step in low temperature ($\sim 80^\circ$C) thermal decomposition in loss of cyanogen.

From this work to date, it would appear that the potential impurities of interest are azido pentaamine cobalt (III) perchlorate, 1-CP, amide (1 and/or 2), amidine, and Co^{++}. Methods of analysis for all these compounds are presently being developed. The overall goal is to be able to analyze a single sample for all these components. The preferred method is HPLC with a specific detector. The work is presently divided into separating these components and achieving a high sensitivity for each component.

G. Separation Methods (M. L. Lieberman)

This work is being conducted by K. E. Bullock (Md), E. A. Deutsch (U.C.), and D. M. Kapsch (Md).

CP and the azido pentaamine cobalt (III) perchlorate can be separated on Eastman K541V polyamide chromagram TLC sheets using 0.01M $HClO_4$ or water as the solvent. The purple azido complex has an R_f of 0.55, while the CP has an R_f value of 0.41. Arrangements have been made to have customized HPLC columns of polymide prepared. On receipt, the separation will be attempted on the HPLC. In the meantime, attempts will be made to separate the amide and Co^{++} from CP on the TLC plates. The results to date indicate that polyamide may be a very favorable support for the separation of CP and its decomposition products.

The azido pentaammine cobalt III, cobalt II and 2-CP can also be separated on a gravity flow Sephadex SP, C-25 cation exchange column using 0.25 M $NaClO_4$ (pH=2) as the eluent. The ability to separate the amide and amidine from CP has not been determined as yet. The drawbacks to use of a Sephadex resin are two fold: (a) Sephadex has been known to oxidize cobalt II to cobalt III and (b) there is no HPLC analog for Sephadex presently available.

Several strong acid cation exchange resins (Biorad AG50W-X8, and Amberlite IRC-50 as well as Chelex 100) were evaluated. Water solutions of CP and cobalt (II) (chosen because of all the species of interest they are the most disimilar and therefore should be most easily separated) were applied to the top of each column and then eluted with 1.0, 1.5, 2.0, 2.5 and 3.0 M NH_4OAc-acetic acid buffers. Neither CP nor Co(II) moved as a distinct band; although, the cobalt (II) could be washed off eventually. It appears that the strong acid cation exchange resins are holding up the CP to a greater extent than would be expected based on charge and size. This phenomenon has been observed previously when attempting to separate complexes containing unsaturated rings. Further evaluation will determine if continued work on this area is justified.

H. Cobalt II Analysis (M. L. Lieberman)

The cobalt II work has been geared to trying to find a nondestructive measure of the cobalt II, trying to increase our ability to see the cobalt II during separation and trying to increase the separability of Co II from CP. The work is being performed at Mound Facility by those individuals mentioned in Section III.G.

Attempts were made to determine the cobalt II levels of CP lot EL47344 using EPR. The determination was made at various temperatures from room temperature to liquid nitrogen and no cobalt II signal was detected. Therefore, at least at the levels found in lot EL47344, EPR does not appear to be useful.

Various methods to increase the separation of cobalt II from CP as well as increase the detection limit for cobalt II are under investigation. Most of these methods involve complexation of Co II to change the size, charge, solubility and extinction coefficient of the complex. One of the more promising of these reagents during preliminary studies was the nitroso R salt (disodium 1-nitroso - 2 - napthol - 3, 6-disulfonate). The nitroso R salt complexes cobalt II in a 3:1 ratio to form a soluble red complex. This is an oxidizing reaction (i.e., the cobalt II is oxidized to cobalt III) which it was felt would protect the CP from decomposition. It was determined using cobalt II chloride solutions that the nitroso R cobalt complex allowed detection of 40 ppm of cobalt II and that a resolution of 20 ppm could be expected; that is, a significant difference in absorbance can be seen between 40 ppm Co II and 60 ppm Co II. The cobalt nitroso R complex obeys Beer's law.

Tests of this reagent were begun on CP solutions: all CP solutions used were 10mg CP/25ml of solution. The nitroso R solution was 4mg/25ml. The following items were observed:

a) at pH7 the absorbance of the cobalt II - nitroso R complex increases with time, which indicates that the CP <u>is</u> degrading at this pH.

b) bromate can be added to destroy excess nitroso-R reagent which results in a sharper peak due to cobalt nitroso R complex (lowers background).

c) if CP/nitroso R solution is kept in a clean closed cuvette, the solution does not change absorbance in the first sixteen minutes; however, during the next fourteen minutes rapid increases in absorbance occur reaching maximum at 30 minutes.

d) lowering the pH to 4 or 5 substantially reduces the rate of CP degradation in nitroso R solutions with no change during the first hour.

e) at pH 4, the reaction of nitroso R with added cobalt is also slowed; however, it appears to be complete within 20 minutes.

Further work will be needed before a decision can be reached on this complex.

I. X-Ray Diffraction (M. L. Lieberman)

Additional x-ray diffraction work is being performed by G. Jendrek (Md), and D. Sullenger (Md).

A theoretical x-ray diffraction powder pattern for CP, based on Graeber and Morosin's single crystal structure was calculated at SLA by Ed Graeber. All of the experimental XRD powder lines for all of the lots (EL47344, EL47345, EL52211, EL58633, EL58636) examined can be matched to lines in the theoretical pattern.

Progress is being made in reconfiguring the Guinier-Simon camera to reliably measure thermal expansion. The microcomputer and new power supply have been delivered. It is optimistically estimated that the delivery of the remaining components, assembly and system checkout will be completed in 1 1/2 months.

J. Infrared Amide Analysis (M. L. Lieberman)

Experiments by C. Kinard (Md) and E. M. Pitre (Md) with various concentrations of CP in DMSO indicated that the solution had to be saturated in order to see any characteristics of a CP spectrum. The liquid cell used for these experiments was a 0.09ml KBr cell with a 0.053mm pathlength. If one assumes lot EL-47344 contained the 3 - 10% amide usually found in CP, this liquid cell technique does not seem promising with present equipment and this solvent system. Further studies of liquid cell techniques will involve trying different solvents, cell sizes, and possibly a different spectrometer.

Nugol mull spectra of this material were also taken. CP was carefully weighed and spiked with known amounts of amide (10 - 90%). It is possible to detect an increase in the amide band, but repeated experiments show that the mull technique is not precise enough for analytical purposes. It may be possible to ratio the nitrile band of CP with the amide band to improve the precision at higher concentrations; but, 3 - 10% amide is near the detection limit of the IR method.

K. HPLC Analysis for Amide Contaminant (V. M. Loyola)

A method by which HPLC (high pressure liquid chromatography) can be used to do the quantitative analysis of amide complex impurity in CP explosive is being investigated. This method differs from previous attempts in that the present technique employs a cobalt (II) reduction step prior to the actual analysis. In previous attempts at using HPLC to do the analysis the efforts made were to separate and quantitate the CP and CP amide impurity; no success was had in these previous efforts due to the enormous difficulty of separating two components which are virtually identical for all practical HPLC purposes.

The present work does not attempt to separate the virtually identical complexes, but instead relies on a prior reduction of the cobalt (III) complexes to liberate the coordinated tetrazoles which, in their unbound state, exhibit significant chemical differences. Analysis of the freed tetrazole ligands is carried out by using a reverse phase bonded phase packing with an aqueous phosphate buffer at pH2.00 as eluent. Using this buffer at pH2.00 provides a mechanism by which the reverse phase packing can operate by causing the 5-cyanotetrazole ($1.6<pK_a<1.7$) and the 5-carboxamidotetrazole ($pK_a = 2.48$) to become protonated and thus to exhibit their organic character. One of the reasons that previous work using reverse phase failed to achieve separation was that, due to the +2 charge on the complexes, the organic character of the complexes was strongly masked. In this work successful separations of the 5-cyanotetrazole and 5-carboxamidotetrazole compounds have been accomplished from both aqueous solutions of decomposed 5-cyanotetrazole (which contains considerable amounts of 5-carboxamidotetrazole as a decomposition product) and from reduced solutions of CP and CP amide.

At the present time the reduction of these complexes is being accomplished by using tin metal to reduce acidified ($HClO_4$) aqueous solutions of the complexes. There appear to be some minor problems with the use of tin to do the job, so there is also some work being done to try and find a suitable alternative to tin reduction. Presently, it appears that CP amide concentrations as low as 1×10^{-4} molar are readily detectable using the Sn reduction method. This corresponds to a 1.04 weight percent amide contaminant in a 1×10^{-2} molar (0.22 g/50 cm^3 solution) CP solution. Attempts are being made to increase the technique's sensitivity.

IV. COMPATIBILITY

Task Leader - T. M. Massis, 2516

Technical Contributors - P. K. Morenus, 2516
R. M. Merrill, 5821
J. T. Healey, 5822
D. H. Huskisson, 5822
J. Reed, Mound

A. Introduction (T. M. Massis)

As in the past (1-4), the primary objective of this task has been to determine the compatibility of various materials; i.e., CP, with materials of construction used in various DDT component designs and studies. Also included are chemical and thermal stability.

Highlights during this period are the completion of the 1078 day Mini-Det sampling, TMA studies with CP loaded steel change holders and thermal measurements of CP/B/$CaCrO_4$ mixtures.

B. Compatibility Results of 1078 day Mini-Det Sampling (T. M. Massis)

The 1078 day Mini-Det sampling has been completed. This program is the major long term compatibility study for CP with typical materials of construction used in various DDT designs. The last sampling was 795 days. Table IV.B.1 is an updated version of the status of the Mini-Det aging program. The original plan was to end this program at 1460 days (4 years). Because of the absence of any problems the intermediate samplings of 970 and 1275 days have been cancelled and the program extended to 5 years. This now provides additional units for the remaining sampling periods.

TABLE IV.B.1

CP MINI-DET AGING PROGRAM

Sampling Period	Date Started	Date Sampled	Tentative Sampling Date
612 Days	2-1-77	10-5-78	Completed
795 Days		4-6-79	Completed
970 Days		Cancelled	Cancelled
1078 Days		1-14-80	Completed
1275 Days		Cancelled	Cancelled
1460 Days			2/81
1825 Days			2/82

There are small isolated crystalline growths containing silver and sulfur on the silver braze. The presence of such crystalline growths have been seen on nearly all other devices that have a silver braze and has been identified as silver sulfide. If any sulfur is present the formation silver sulfide will eventually occur and is in no cause for alarm. The extent does equilibrate with time. It can be said that the Mini-Dets headers look similar to all previously examined units and no problems exist.

Co^{+2} analyses of the CP removed from the Mini-Dets are listed in Table IV.B.2. Also included are the analyses for the 612 and 795 day samplings for comparison. From these data no significant variation of the current sampling compared to past can be observed. At 80°C or below the values average 800-850 ppm Co^{+2} or less, except for one of the 60°C samples. No change with time appears to be occurring. At 120°C a definite reaction in the CP has taken place with the Co^{+2} contents above 4000 ppm. The CP has a light green yellow color to it compared to the pure yellow color in the 80°C or lower samples. It appears that the amount of Co^{+2} formation has equilibrated with time. The 612,795 and 1078 day values are for the most part similar. Based upon these data, CP does not indicate any measurable instability at temperatures of 80°C or below. The error bars on the 1078 day data were repeated absorbance measurements on different samples from the same volumetric flask. These data indicate that an average value of 800 ppm Co^{+2} may be the lower limit of sensitivity by this method.

TABLE IV.B.2

Co^{+2} ANALYSIS OF CP REMOVED FROM
AGED MINI-DETS

	ppm Co^{+2} present after aging		
Environment	612 Days	795 Days	1078 Days
Room Temp.	166	301	456 ± 215
	334	630	778 ± 209
	<87		
	<85		
60°C	254	383	639 ± 169
	93	355	1370 ± 134
	313		
80°C	299	461	463 ± 93
	824	542	839 ± 171

TABLE IV.B.2 (cont'd)

Environment	612 Days	795 Days	1078 Days
120°C	3710	3070	3160 ± 218
	2270	4557	4180 ± 138
	2700		
	3150		

Thermal analysis of the aged powders, performed using both isothermal and non-isothermal techniques, to obtain kinetic parameters show no differences between the aged CP and baseline samples. These data are also similar to previous data obtained on 612 and 745 day samples. The decomposition products do not appear to alter the reaction kinetics in aged CP.

C. Thermo-mechanical Analysis (T. M. Massis)

The last two reporting periods have described a thermo-mechanical analysis procedure which measures the coefficient of thermal eppansion for CP plus provide data about the possibility of CP decoupling from the bridgewire/pin interface under high force environments. Such a procedure has been used successfully to simulate such decoupling problems in the MC2949 using the pyrotechnic $TiH_{.65}/KClO_4$.

The previous work used CP in a ceramic charge holder assembly. No movement of the CP in relation to the stationary charge holder was observed. Therefore, no decoupling from the bridgewire/pin interface would be expected.

Since the MC3196 uses a stainless steel 304 charge holder, the TMA procedure was repeated with this charge holder material loaded with CP. The CP was loaded at Unidynamics at 10 and 25 kpsi consolidation pressures. For the three (3) units loaded at 10 kpsi, no slippage of the CP in relation to the stationary charge holder was observed for repeated cycles from -50 to 125°C.

One of the four units loaded at 25 kpsi did result in slippage of CP at the end of the third cooling cycle but at temperature below -100°C. Slippage would not have occurred if the unit was cooled to the usual -50 to -75°C. The resulting TMA trace does not indicate any slippage in the -50 to -75°C range. Once the heat cycle starts pellet slippage never occurs because of the greater expansion of the CP compared to the charge holder material. The other three units behaved normally during the TMA test.

In the normal operating range (-50 to 125°C) decoupling problems with CP with either a ceramic or stainless steel charge holder are not expected when the forces are less than 1000 "G's".

D. Thermal Properties of CP and Mixtures with B/$CaCrO_4$

(M. L. Lieberman)

Studies in this area are being performed by J. Reed (Mound).

Isothermal DSC work was done on CP and mixtures with B/$CaCrO_4$ on a Perkin-Elmer differential scanning calorimeter model DSC-2. The DSC runs were made in closed, vented containers. The venting was accomplished with an approximately 1 mm hole in the container lid. The DSC isothermal runs were carried out by dropping the sample and container onto the previously heated DSC. Typically a sharp endotherm is observed as the sample and container are heated to isothermal conditions. A typical 520 K isotherm is shown in Figure IV.D.1. Zero time is arbitrarily chosen as the time at which the sample is dropped onto the DSC. Figure IV.D.1 is typical of all the DSC isothermal runs with vented containers, both with CP and with mixtures. Long time intervals are observed during isothermal runs before any observable exothermal reaction is encountered. The delay times to exotherm decrease with increased isothermal temperature and the peak height increases. The delay time is chosen as the time from sample drop to the initiation of an observable exothermic peak. A correlation of delay time with isothermal temperature is shown in Figure IV.D.2 where delay time is plotted against reciprocal temperature.

Attempts have been made to analyze the data from these vented isothermal DSC experiments. The delay data can be fitted nicely to an Arrhenius equation where the loss of reciprocal delay time is a function of reciprocal temperature. This correlation, however, says nothing about reaction rate or rate of release of energy as a function of temperature. An attempt was made to obtain rate constants, reaction orders and activation energies for the exothermic reaction process.

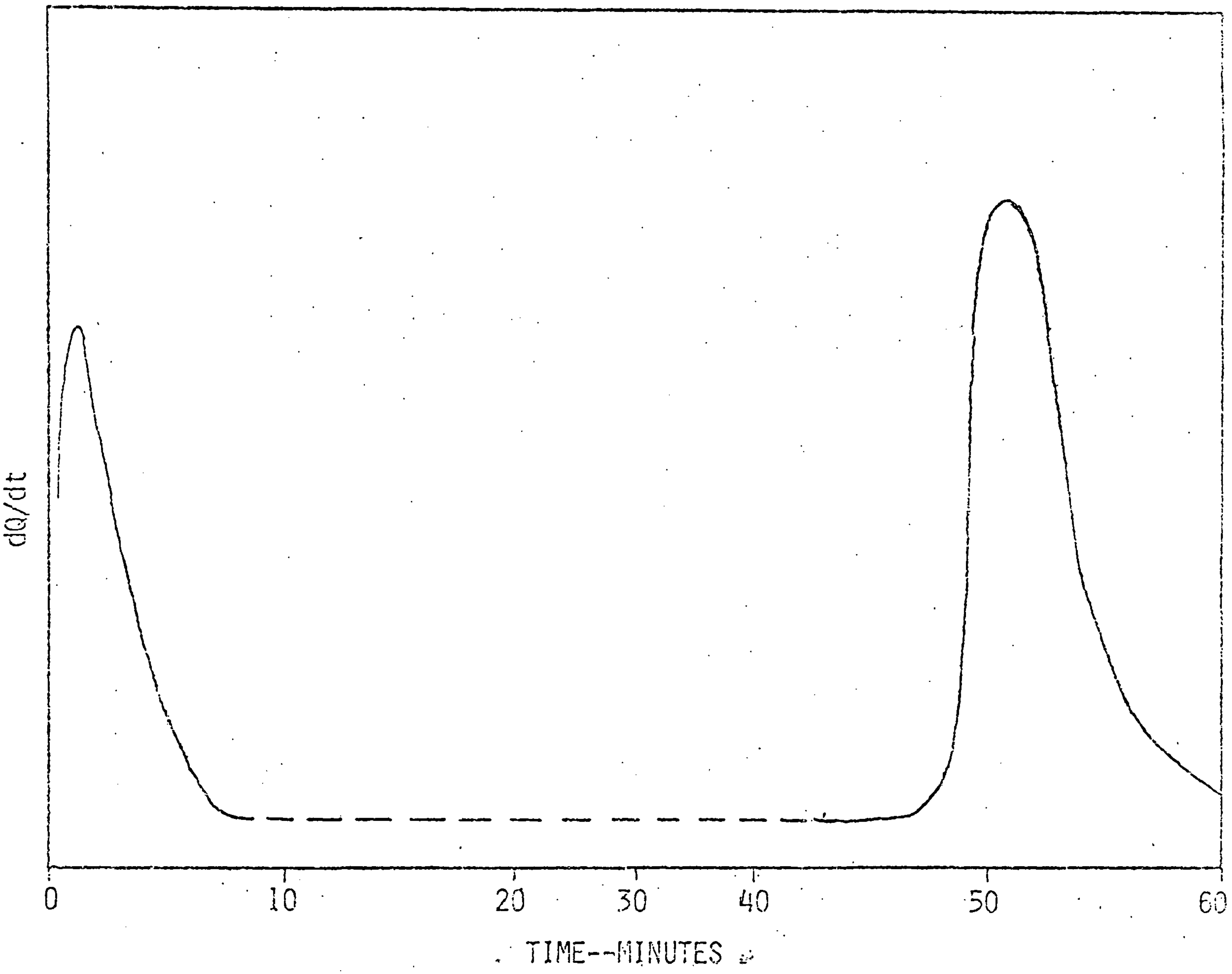


FIGURE IV.D.1 A Typical Isotherm for $CP/B/CaCrO_4$ at 520 K

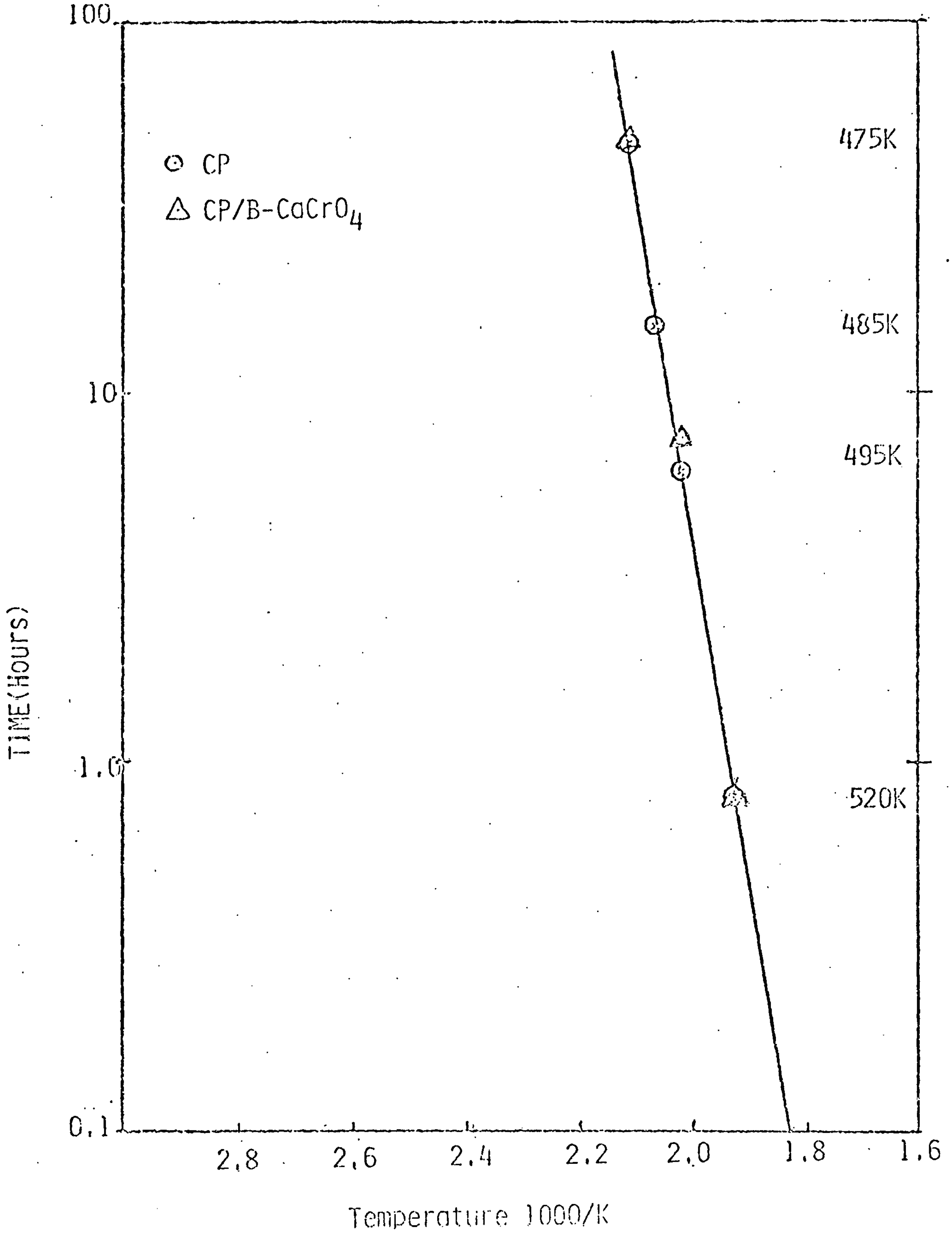


FIGURE IV.D.2 Exothermal Delay Time vs. Temperature for CP/B/CaCrO$_4$ and CP

For each DSC isotherm an order plot was obtained and the rate constant was calculated for the region of relatively constant order (n). A typical order plot for the 475 K CP isotherm is shown in Figure IV.D.3 from which a rate constant of 0.077 cal/sec/g was obtained. An order plot for the CP mixture with B/$CaCrO_4$ is shown in Figure IV.D.4.

The kinetic parameters calculated for CP from isotherms over the temperature range 475 - 520 K are shown in Table IV.D.1 and the calculated parameters for the CP mixture with B/$CaCrO_4$ are shown in Figure IV.D.5 for both CP and the mixture.

The activation energy calculated for the CP exothermic reaction is 31 Kcal/mole with ln(A) = 30.4 while the activation energy for the mixture is 37 kcal/mole (CP) with ln(A) = 36.6 for data in mcal/sec/mg. Within the precision of the data the mixture is not different from the CP as seen from Figure IV.D.5 where ln(k) is plotted versus reciprocal temperature.

The activation energy for delay is 44 Kcal/mole with ln(A) ln(A) = 39.4 for data in reciprocal time.

Isothermal runs with ammonia flow gas were initiated to determine the effect of ammonia on the CP decomposition and exothermic reaction. The runs were made on a Mettler thermobalance with a corrosive furnace using open sample containers. Blank CP runs without ammonia correlated well with the DSC isothermal work. A typical isotherm is shown in Figure IV.D.6 for 235°C. Both DTA and TGA are shown indicating both a delayed exotherm and a simultaneous weight loss for runs without ammonia. In the same figure an ammonia

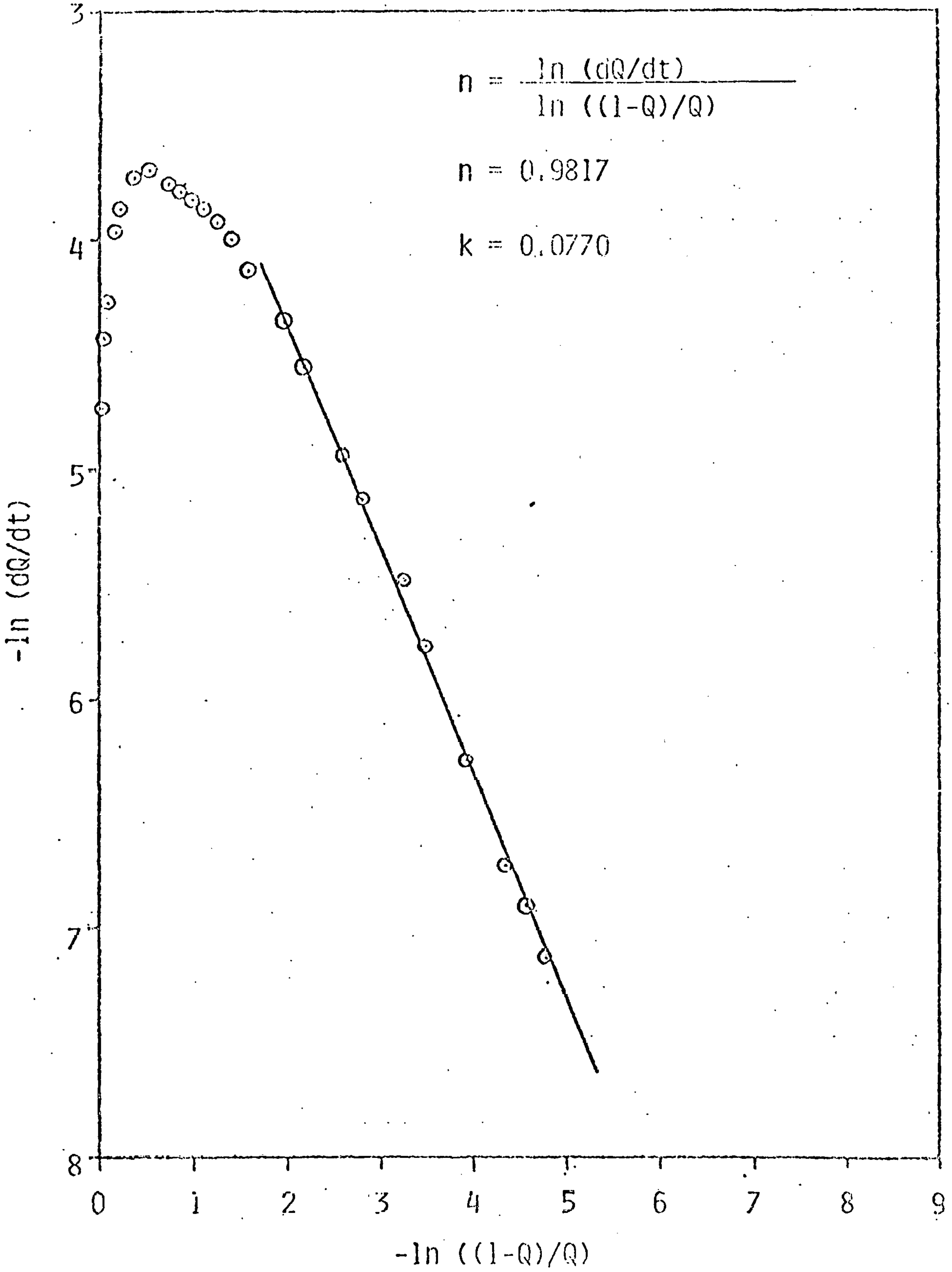


FIGURE IV.D.3 Determination of Reaction Order for CP at 475 K

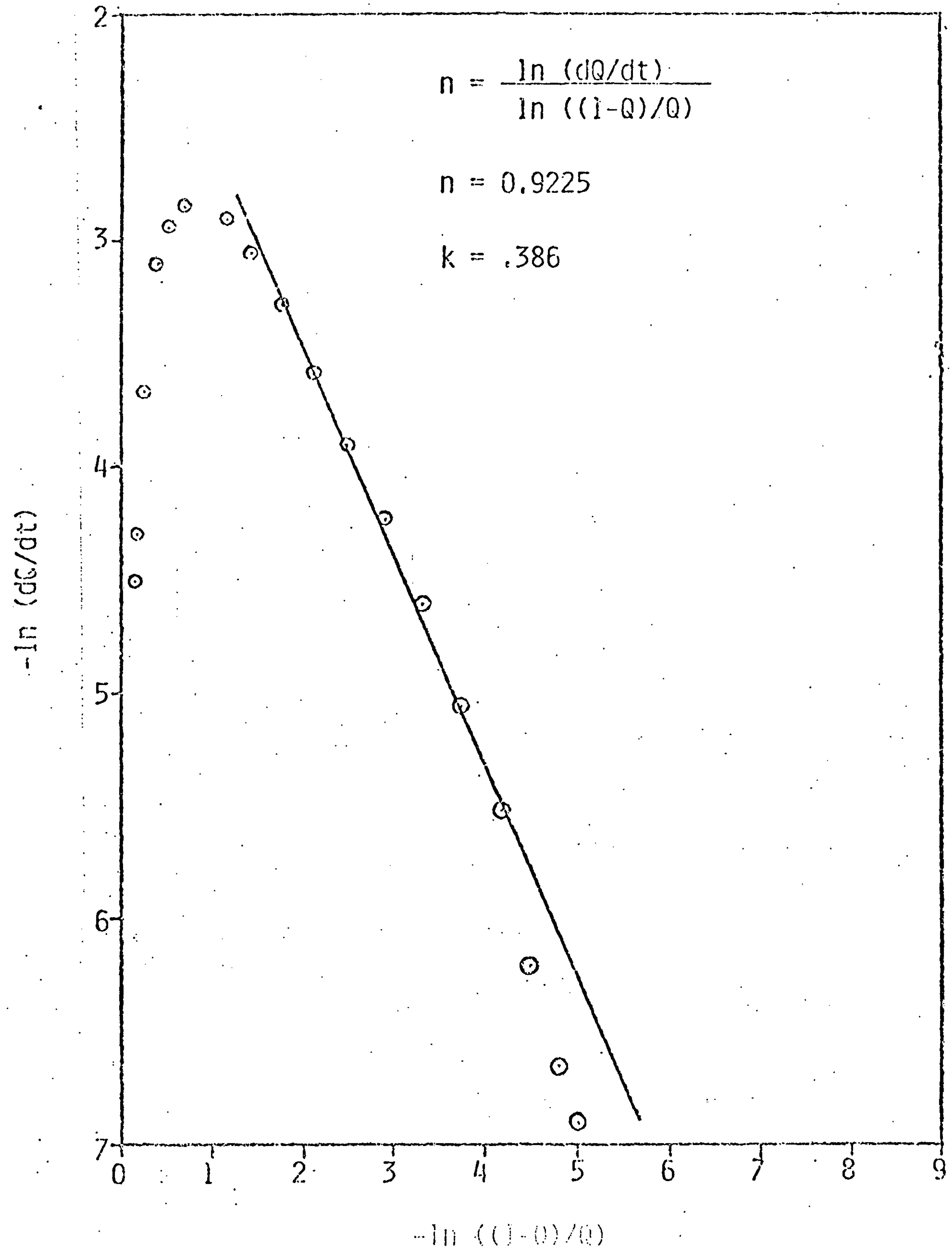


FIGURE IV.D.4 Determination of Reaction Order for CP/B/$CaCrO_4$ at 495 K

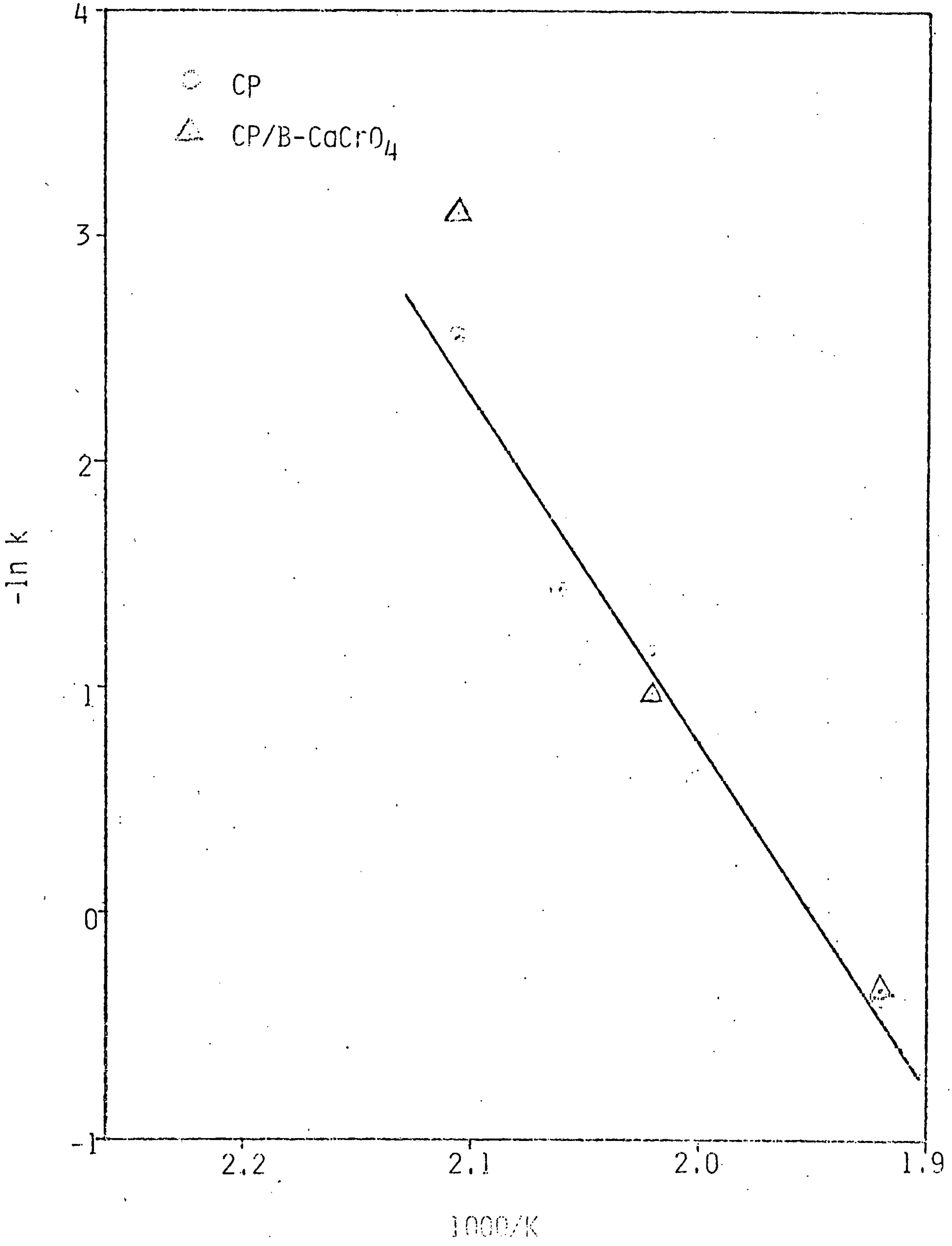


FIGURE IV.D.5 CP Rate Constant Plot

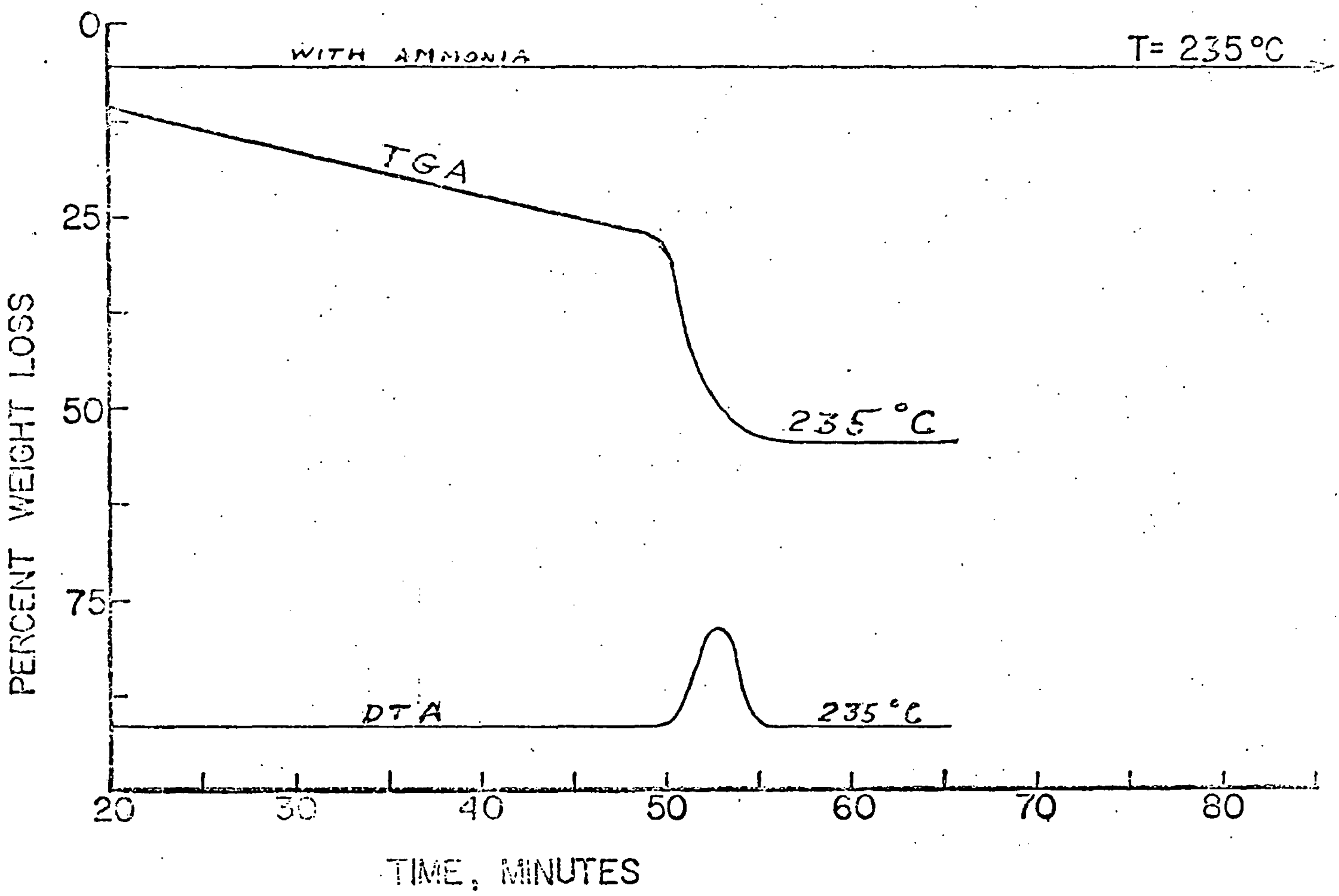


FIGURE IV.D.6 Effect of Ammonia cn Thermogram of CP run shows no exotherm and no weight loss. With ammonia flow gas at 235°C the temperature was held for greater than 8 hours without weight loss or observable exotherm.

The limited work done so far supports the hypothesis that ammonia suppresses both decomposition and the exothermic reaction of CP. Work with ammonia and CP will continue to higher temperature and will determine if the reaction can be initiated after removal of ammonia flow gas on runs of significant duration. Work will continue on the modulated molecular beam mass effusion cell work and to determine if other species can be observed and measured at relatively low temperatures, typically between room temperature and 140°C. Work will also continue on kinetic parameters for CP as time permits.

TABLE IV.D.1

CP KINETICS PARAMETERS

K	1000/K	n	k	-lnk	t (min)
475	2.105	0.982	0.077	2.560	2740
485	2.062	1.150	0.239	1.430	900
495	2.020	0.945	0.317	1.150	391
520	1.923	0.750	1.520	-0.418	48

TABLE IV.D.2

CP/B-$CaCrO_4$ KINETICS PARAMETERS

K	1000/K	n	k	-ln(k)	t (min)
475	2.105	0.873	0.045	3.110	2832
485	2.062				
495	2.02	0.923	0.386	0.952	450
520	1.923	0.902	1.410	-0.341	48

V. COMPONENTS

Task Leader - M. L. Lieberman, 2515

Technical Contributors - R. O. Brooks, 1541
T. E. Demaree, 1541
D. L. Marchi, 2515
F. J. Villa, 2515
D. R. Schaeffer, Mound
C. E. Gallaher, Mound
L. W. Wise, Mound
R. Slape, Pantex
A. Lause, Unidynamics

A. MC3533 Detonator (M. L. Lieberman)

An investigation of bridgewire ignition sensitivity has been performed at Unidynamics. MC3089 headers were utilized with 0.0015 and 0.0016 inch diameter Tophet A bridgewires and CP explosive consolidated in two increments at 40 kpsi.

A summary of the ignition sensitivity results are given in Tables V.A.1 and V.A.2. The results indicate that either bridgewire can be used to achieve a satisfactory no-fire condition, as well as reliable ignition from a 10 mJ, 2.5 μs source. The 0.0016 inch diameter bridgewire has been selected for use in the MC3533 detometer.

A design matrix has been defined and is under investigation. Parameters included are igniter loading pressure (40 and 70 kpsi), igniter loading dwell time (10, 30, and 60 seconds), charge holder length (0.197 - 0.400 inch), and output measurement (witness plate dent with and without a PETN output pellet). A purchase order for MRS requirements has been placed.

TABLE V.A.1

IGNITION SENSITIVITY TESTS

BW Diameter	0.0015 Inch BW	0.0016 Inch BW
Test	Langlie No-Fire Sensitivity	
n	10	10
$\bar{I}$, amps	1.284	1.3097
σ, amps	0.0225	0.0747
I (99.9% lower limit, 95% confidence), amps	---	0.7984
Test	Langlie All-Fire Sensitivity	
n	10	10
$\bar{E}$, mJ	4.421	3.100
σ, mJ	0.591	---
E(99.9% upper limit, 95% confidence), mJ	8.72	---
Test	Langlie Test Survivors (10mJ, 2.5 μs)	
$\bar{t}_F$, μs	12.67	11.27
σ, μs	1.22	1.04
Fires	10	10
No-Fires	2	0

TABLE V.A.2

FUNCTION TIME DATA

Firing Temperature	0.0015 Inch BW			0.0016 Inch BW		
	n	$\bar{t}_F$, μs	σ, μs	n	$\bar{t}_F$, μs	σ, μs
-60°F	5	10.70	1.29	5	11.98	1.56
Ambient	2*	10.25	0.778	4	10.62	0.41
+140°F	2	10.58	0.65	5	9.74	0.44

*Testing of the group resulted in two lost data incidents. Of three for which there are data, one resulted in an uncharacteristically long function time, which was eliminated from the statistical population.

B. CP Powder Shock Tests (D. L. Marchi)

The MC3533 explosive detonator will use the explosive CP and experience a g load force of approximately 10,000 g and an approximate duration of 1 millisecond. The explosive CP has not been previously shock tested to this level; therefore it was appropriate to test and obtain preliminary information on its shock behavior prior to committing its use in a system subject to a shock environment.

Mechanical shock testing to determine the sensitivity of the explosive CP was conducted on December 13, 1979. Richard O. Brooks and Terry E. Demaree, Organization 1541A, instrumented and conducted the testing. The existing air gun facility, building 6710 in Area III, was available and required no modifications to provide the mechanical shock conditions required. A safe operating procedure was drafted and all testing was performed under its guidelines.

Six shock vessels, compatible with the design of the air gun, were built and each was loaded with approximately 116 mg of CP powder. The CP used was from engineering lot EL-47344 and was loaded at 10 kpsi in a series of increments ($\ell/d \simeq 0.5$).

Mechanical shocking was accomplished by impacting a ram piston into the fixture assembly which contained the test specimen vessel. The 1 1/2 inch diameter ram piston was driven through a 64 inch long barrel pressurized to 280 psig. An Endevco Model 2264-30KR accelerometer was installed in the down-stream end of the shock piston. This, along with break wires made of stretched solder wire, provided acceleration versus time data. Image motion photography was used to measure velocity of the ram at and after impact. This generated check data which verified the information obtained from the accelerometer and break wires.

Four of the shock vessels were subjected to a longitudial axis haversine shock pulse averaging 13,600 g; shock duration time typically was 0.9 ms. The remaining two shock vessels were shocked in a radial axis. The pulse was identical in amplitude and duration to the other tests. Each explosive specimen was only shocked once.

None of the explosive samples subjected to testing detonated. There was no evidence of degradation of the powder or signs of ignition. All sample test vessels have been returned to Organization 2515 for possible further examination and disposal.

Additional technical information on these shock tests is given by R. O. Brooks and T. E. Demaree, 1541A, in Sandia Environmental Test Report R801540 entitled "Mechanical Shock Tests on CP Powder Specimens".

C. CP Detonator Development (M. L. Lieberman)

Functional testing of CP detonators similar to the MC3533 is being performed by D. R. Schaeffer and L. J. Wise (Mound). The effects of density and length of the CP powder column on output and function time are being determined. This effort is divided into three parts. In the first part, the density is constant through the entire charge length (0.120 to 0.600 inches) with values of 1.5, 1.6, or 1.7 Mg/m^3. The second part utilizes a 0.120 inch long ignition zone at a density of 1.7 Mg/m^3 with the remainder of the CP column (0.240 to 0.480 inches) at a density of either 1.5 or 1.6 Mg/m^3. The last portion of the test uses a 0.120 inch long ignition and output charge at 1.7 Mg/m^3 with the center or transfer portion of the charge (0.120 to 0.360 inches) at a density of either 1.5 or 1.6 Mg/m^3.

A sketch of the development detonator used in the study is shown in Figure V.C.1. Function time was to be measured by an ionization finger switch; however, the switches failed to give reliable information during the first tests and will be replaced. Output information is obtained by measuring the dent produced in cold rolled steel witness blocks.

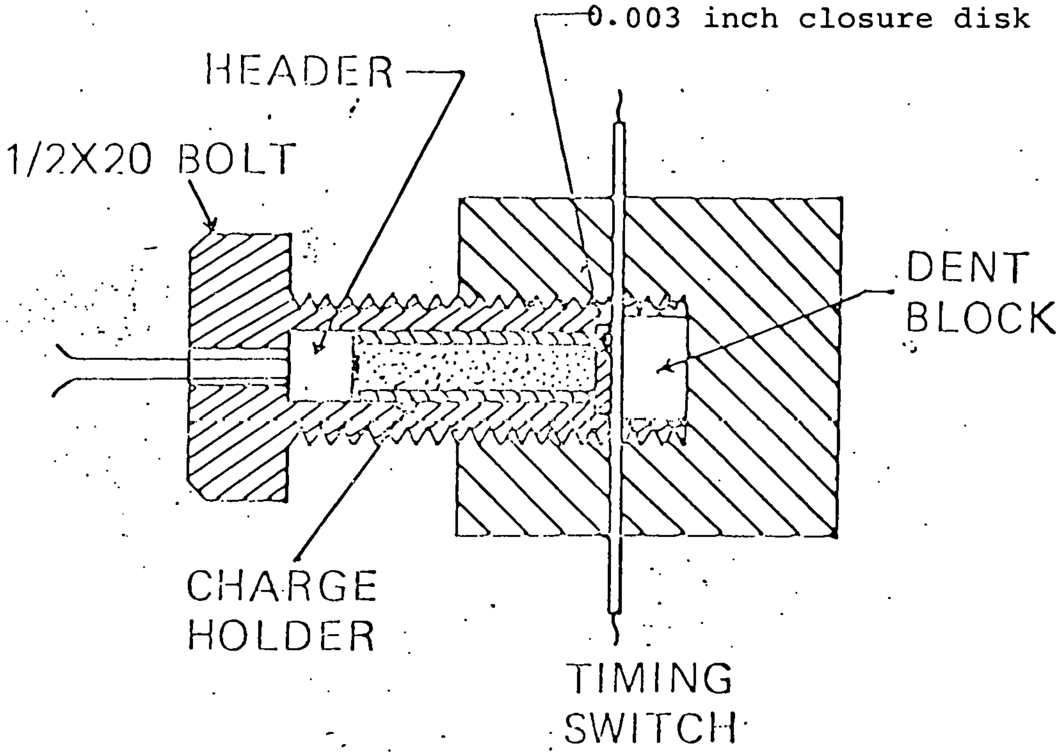


FIGURE V.C.1 Sketch of the CP test detonator. Charge lengths of 0.120 to 0.600 inches in 0.120 inch increments will be tested. The diameter of the CP charge is 0.120 inches and is loaded in 0.060 inch increments.

Twenty-two test detonators were fired and the results are summarized in Tables V.C.1-3. These results are preliminary and require further testing to define trends; however, there is an obvious reduction in output when a density of 1.7 Mg/m^3 is maintained through the entire detonator.

Future testing will determine the lengths of 1.5 Mg/m^3 density required for detonation (with and without 1.7 Mg/m^3 density in the ignition and output zones), provide a comparison of uniform 1.5 and 1.6 Mg/m^3 densities, and investigate the behavior of densities less than 1.5 Mg/m^3.

TABLE V.C.1

OUTPUT DATA FOR TESTS UTILIZING UNIFORM DENSITY

Density[b], Mg/m^3				
Average	Max	Min	Length (in)	Dent Depth (mils)
1.48	1.49	1.47	0.120	3.2
1.48	1.51	1.45	0.120	3.6
1.47	1.53	1.40	0.600	21.8
1.51	1.54	1.49	0.600	22.2
1.49	1.53	1.44	0.600	17.7
1.61	1.64	1.58	0.360	8.7
1.57	1.58	1.55	0.360	14.1
1.60	1.70	1.66	0.120	1.8
1.64	1.65	1.63	0.120	2.3
1.69	1.73	1.64	0.600	5.1
1.68	1.69	1.67	0.600	3.4

[a] Dent made in cold rolled steel (hardness - Rockwell B90) through 0.005 in closure disk.

[b] The CP was loaded in 0.060 inch increments. The maximum and minimum densities of these incremental loadings.

TABLE V.C.2

OUTPUT DATA FOR TESTS UTILIZING A DENSITY OF ABOUT 1.7 Mg/m^3 IN THE IGNITION ZONE

Density[b], Mg/m^3				
Average	Max	Min	Length (in)	Dent Depth (mils)
1.63/1.51	1.68/1.53	1.59/1.50	0.600	23.0
1.71/1.51	1.72/1.53	1.71/1.47	0.600	16.3
1.66/1.50	1.66/1.52	1.65/1.46	0.600	22.3
1.72/1.60	1.75/1.61	1.70/1.59	0.360	4.7
1.68/1.62	1.69/1.63	1.67/1.60	0.360	4.9

[a] Dent made in cold rolled steel block through 0.005 inch closure disk.

[b] Density information format is: Ignition Zone Density/Output Zone Density. Maximum and minimum densities refer to the range of the 0.060 inch incremental loadings of CP.

TABLE V.C.3

OUTPUT DATA FOR TESTS UTILIZING A DENSITY OF ABOUT 1.7 Mg/m^3 IN THE IGNITION AND OUTPUT ZONES

Density[c], Mg/m^3				
Average	Max	Min	Length (in)	Dent Depth (mils)
1.76/1.47/1.66	1.78/1.49/(a)	1.73/1.44/(a)	0.600	19.0
1.70/1.51/1.67	1.70/1.54/1.70	1.70/1.48/1.66	0.600	17.9
1.66/1.49/1.68	1.73/1.51/(a)	1.59/1.46/(a)	0.600	20.9
1.69/1.58/1.66	1.72/1.60/1.68	1.66/1.57/1.64	0.360	5.4
1.74/1.61/1.66	1.75/1.62/(a)	1.73/1.60/(a)	0.360	6.3
1.75/1.53/1.71	1.78/1.63/(a)	1.72/1.61/(a)	0.360	5.3

[a] Individual determinations of two loadings were not made - only the average is known.

TABLE V.C.3 (con'td)

[b] Dent made in cold rolled steel block through 0.005 inch closure disk.

[c] Density information format is:

Ignition Zone Density/Transfer Zone Density/Output Zone Density. Maximum and minimum densities refer to the range of the 0.060 inch incremenial loadings.

D. MC3423 Detonator (M. L. Lieberman)

A series of tests of the MC3423 detonator have been performed with next assembly units. These tests have been performed under various thermal conditions and using next assembly units fabricated at Sandia and GEND. It has been shown that units fabricated in the two facilities exhibit significantly different responses. Consequently, it is desirable to increase the output of the detonator. By filling the cavities beyond the output charges with XTX-8003 provided by R. Slape (Pantex), the output has been significantly increased, as shown by several tests.

E. MC3196A Detonator (F. J. Villa, M. L. Lieberman)

The MC3196A detonator is being developed as a replacement for the MC3196 detonator and will be treated as an in-process change, rather than as a new component. It will be geometrically identical to the existing device, but have a function time of at least 50 μs when subjected to a 10 mJ, 2.5 μs ignition pulse. The MC3196A presently functions in approximately 20 μs.

Previous reports (4,5) have given feasibility results obtained for various materials in the igniter region of the detonator. While mixtures of B/$CaCrO_4$/CP had shown some encouragement for obtaining a function time of 50-200μs, additional work, shown in Figure V.E.1 has shown considerable scatter in this region. Consequently, it is felt that such mixtures cannot yield a 50-200μs function time with high reliability.

Several tests were performed with barium styphnate loaded in the igniter at 25 kpsi. Burn times of 1180 and 1250 μs/in were obtained. While these values appeared suitable, no further work is anticipated because the material is not presently qualified for Sandia components.

Instead, it was decided that a longer delay time, which could be achieved with qualified materials, was preferable. It was found that this could be achieved by loading a layer of B/$CaCrO_4$ against the bridgewire and following that with the explosive CP. Igniters were loaded with 3-8 mg of B/$CaCrO_4$ to yield pads (15 kpsi) of 0.010-0.025 inch thickness. They were then loaded with two increments of CP at 15 kpsi. The effects of the pad size on function time and resistance-after-fire (RAF) are shown in Figures V.E.2 and V.E.3. Note that the minimum resistance in the latter figure occurred at the completion of B/$CaCrO_4$ combustion. Three additional tests were performed with transfer charges to ascertain that suitable growth to detonation occurred and that no RAF problem was

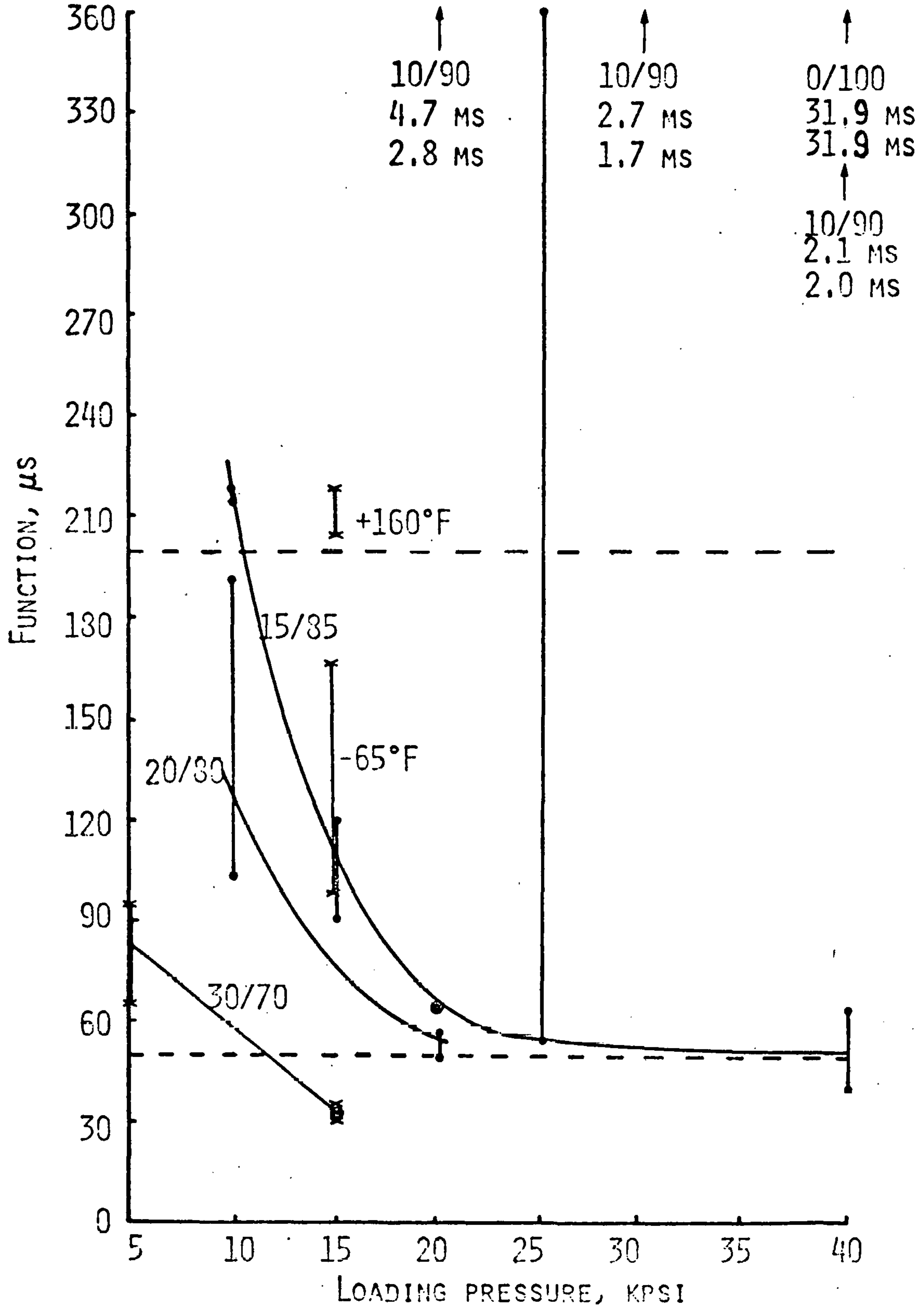


FIGURE V.E.1 Function Times for CP/B/$CaCrO_4$ Mixtures

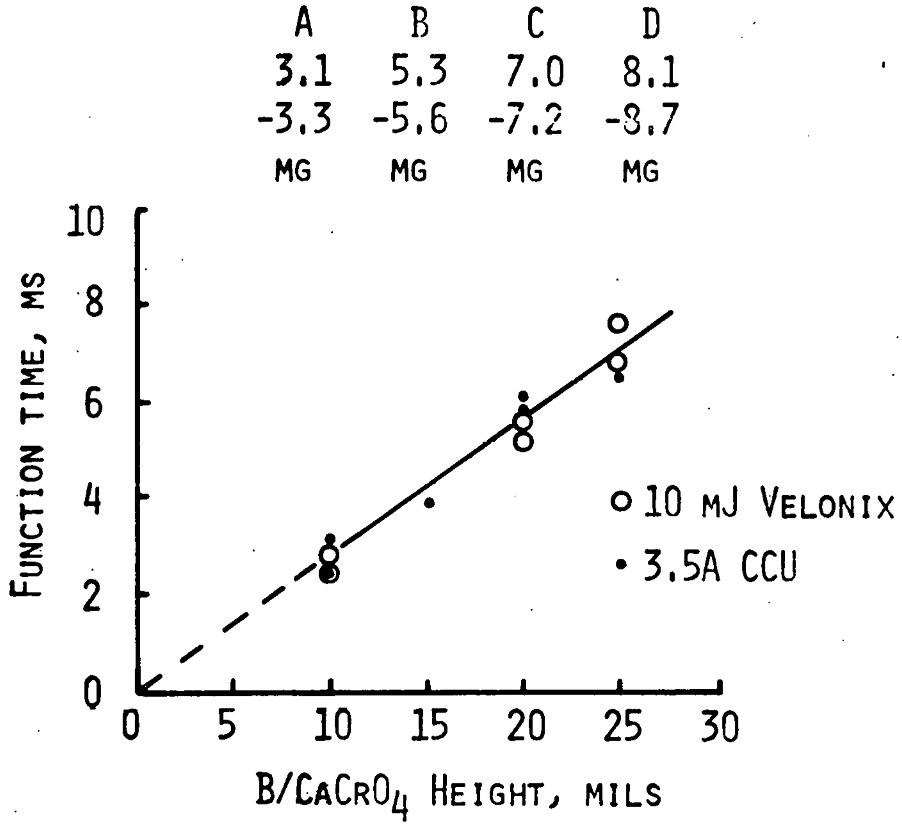


FIGURE V.E.2 Function Time versus B/CaCrO$_4$ Pad Height

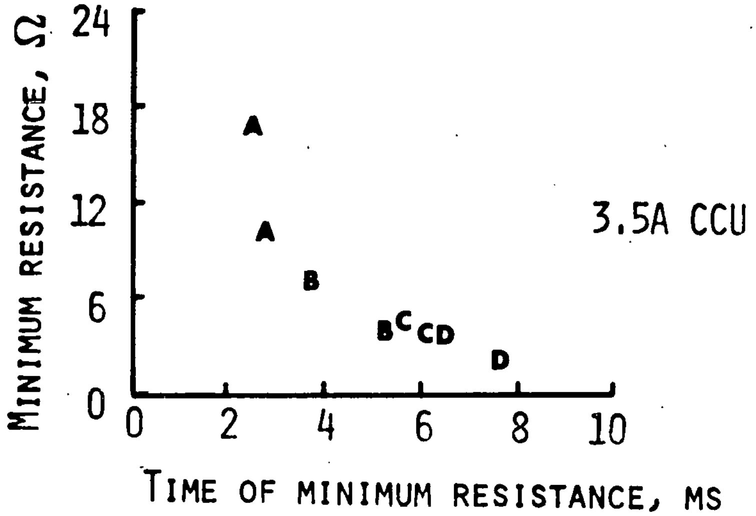


FIGURE V.E.3 Minimum Resistance versus Time for Various B/CaCrO$_4$ Pad Heights so introduced. The data shown in Table V.E.1 show these results.

From these results and discussions with Unidynamics production personnel, it was decided that a B/$CaCrO_4$ pad of 5±0.5 mg was suitable. The 0.0012 inch diameter bridgewire used in the MC3196 was originally designed to ignite B/$CaCrO_4$ with a 10 mJ, 2.5 μs pulse, and this bridgewire/powder system is presently used in the MC2943 MC2987, and MC3089. Purchase order 49-1786 has been placed with Unidynamics for development support in the areas of fabrication and testing of development components. Table V.E.2 summarizes tests required by the subject contract. Item 1 has been completed. Dents in witness plates ranged from 0.014 to 0.0175 inch. Since the MC3196A is to utilize dent blocks to measure output, rather than the PXD-S pressure transducers used for the MC3196 (as a cost saving change), these dent values can be compared with those to be obtained from the delay detonator to ascertain that comparable output has been achieved. Table V.E.3 describes ignition sensitivity testing to be performed.

The MC3196A will be incorporated into production in lot 5 which is expected to start in September or October, 1980. Consequently, a rapid development program is planned, as shown in Table V.E.4.

TABLE V.E.1

MC3196A IGNITER/TRANSFER ASSEMBLY

RAF AND OUTPUT STUDY

BRIDGE CHARGE: $B/CaCrO_4$ (15 kpsi)
IGNITER OUTPUT: CP, 30-31 MG (15 kpsi)
TRANSITION CHARGE: CP, 88-89 MG (10 kpsi)
FIRING MODE: 3.5 AMPERES

S/N	$B/CaCrO_4$		MINIMUM RESISTANCE TO 200 MS		OUTPUT	
	COLUMN HEIGHT INCH	CHARGE WEIGHT MG	R, OHMS	T, MS	T, MS	DENT, INCH
87	0.013	4.9	12.101	3.90	4.351	0.012
88	0.014	5.1	4.622	4.80	4.712	0.013
89	0.013	4.7	10.943	3.70	4.153	0.011

TABLE V.E.2

MC3196A DELAY DETONATOR

DESIGN VERIFICATION TEST PROGRAM

TASK	QTY	100%			IGNITION				OUTPUT			
		ETR	X-RAY	LEAK	B/W BREAK	3.5 AMP	10MJ 2.5µS	RAF	FUNCTION TIME	DENT BLKS	PXD-S	ENVIRONMENTAL SEQUENCE
1. D-TEST 10 EACH MC3196 DETS WITH DENT BLOCKS	10					✓			✓	✓		
2. BUILD 35 EACH DELAY DETS FOR ENVIRONMENTAL SEQUENCE & OUTPUT TEST	35(4)	(1) ✓	✓	✓	✓	15	20	✓	✓	30	5	30
3. BUILD 255 DELAY IGNITORS 40 DET SUB-ASSY'S	255	✓										
4. PERFORM IGNITION SENSITIVITY TESTS	190	✓			✓	(3) ✓	✓	(2) ✓	✓			
5. BUILD 40 DELAY DETS FOR ENVIRONMENTAL SEQUENCE & OUTPUT TESTS	40	(1) ✓	✓	✓	✓	20	20	✓	✓	40		30

(1) ETR TO BE PERFORMED AFTER EACH ENVIRONMENT

(2) NO-FIRE DETONATOR SUB-ASSEMBLY UNITS ONLY

(3) CONSTANT CURRENT AS REQUIRED

(4) IGNITORS FOR THIS LOT LOADED IN DEVELOPMENT. SUBSEQUENT BUILDS PERFORMED IN PRODUCTION.

TABLE V.E.3

MC3196A IGNITION TESTS

TEST	QTY	TEST UNIT CONFIGURATION	TEST ENERGY SOURCE	TEST LIMITS (AMPERES)
ALL-FIRE	40	IGNITOR	10MS CONSTANT CURRENT(1)	HI: LO:
NO-FIRE/ ALL-FIRE	40	IGNITOR	200MA FOR 5 MIN THEN 10MS CONSTANT CURRENT(1)	HI: LO:
ALL-FIRE	40	IGNITOR	2.5μS, VELONEX(1)	HI: LO:
NO-FIRE	40	DETONATOR SUB-ASSEMBLY	5 MINUTE CONSTANT CURRENT(1)	HI: LO:
CURRENT VS FUNCTION TIME	30	IGNITOR	CURRENT LEVELS FOR 10MS OF 3.5, 5, 10, 25, 50, 100	N/A

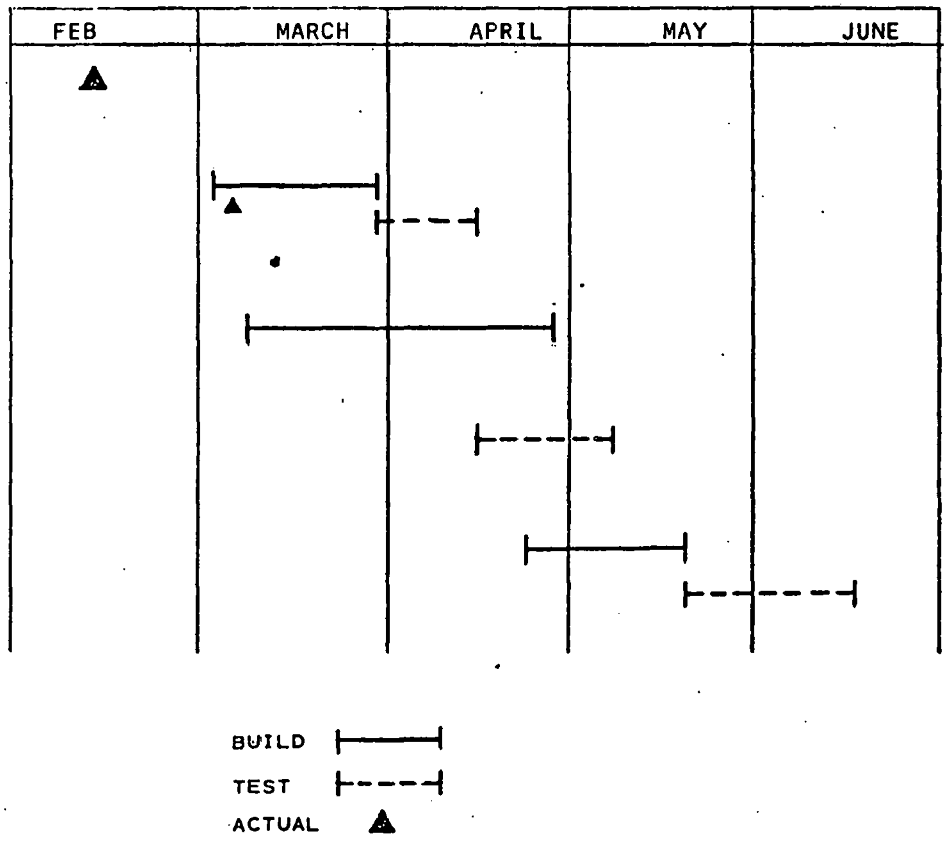
(1) VARIATION IN THE FIRE PULSE ACCORDING TO THE ONE-SHOT LANGLIE METHOD

TABLE V.E.4

MC3195A DELAY DETONATOR
SCHEDULE

<u>TASKS</u>

1. D-TEST 10 EACH MC3196 DETS WITH DENT BLOCKS
2. BUILD 35 EACH DELAY DETS FOR ENVIRONMENTAL SEQUENCE & OUTPUT TEST
3. BUILD 255 DELAY IGNITORS AND 40 DET SUB-ASSY'S
4. PERFORM IGNITION SENSITIVITY TESTS
5. BUILD 40 DELAY DETS FOR ENVIRONMENTAL SEQUENCE & OUTPUT TESTS



VI. REFERENCES

1. M. L. Lieberman, ed., "The Deflagration-to-Detonation Transition Project: Quarterly Report for the Period September through November 1978, "SAND78-2409, RS2515/132, February 1979; also, M. L. Lieberman, ed., Quarterly Report for the Period September Through November 1978," SAND79-0837, April 1979.

2. M. L. Lieberman, ed., "The Deflagration-to-Detonation Transition Project: Quarterly Report for the Period December 1978 Through February 1979," SAND79-1267, June 1979.

3. M. L. Lieberman, ed., "The Deflagration-to-Detonation Transition Project: Quarterly Report for the Period March 1979 Through May 1979," SAND79-1952, October 1979.

4. M. L. Lieberman, ed., "The Deflagration-to-Detonation Transition Project: Quarterly Report for the Period June Through August 1979," SAND80-0230/1, January 1980; also SAND80-0230/2, RS2515/80/6, April 1980.

5. M. L. Lieberman, ed., "The Deflagration-to-Detonation Transition Project: Quarterly Report for the Period September Through November 1979," SAND80-1157, July 1980.

6. O. L. Burchett, R. W. Dietzel, and A. P. Montoya, "The Compaction Behavior of Ten Pyrotechnic Materials," SAND79-1833, January 1980.

Unlimited Release

Distribution:

Combustion Sciences, Inc.
208 Elmwood Road
Champaign, IL 61820
Attn: H. Krier

Mound Facility (11)
P. O. Box 32
Miamisburg, OH 45342
To: A. Attalla
K. Bullock
L. W. Collins
R. J. DeSando
C. E. Gallaher
E. Jendrek
J. Mohler
T. G. Nelson
D. Schaeffer
H. L. Turner, attn: J. R. Brinkman
R. A. Fischbein
M. A. Woltermann, attn: W. D. Pardieck

Naval Surface Weapons Center
White Oak, Silver Spring, MD 20910
Attn: C. Laib

Unidynamics/Phoenix, Inc. (4)
P. O. Box 2990
Phoenix, AZ 85062
Attn: J. Fronabarger
A. Lause
R. Smith
D. Yates

1415 J. T. Hillman, attn: L. Learson
R. Zottnick
1533 R. A. Benham
1556 S. A. Ingham, attn: E. A. Igel
2500 J. C. Crawford
2510 D. H. Anderson
2513 J. E. Kennedy, attn: R. J. Burnett
R. W. Dietzel
A. K. Jacobson
W. B. Leslie
D. J. Mullikin
2513 P. L. Stanton
2514 B. H. Van Domelen, attn: G. J. Janser
2515 P. D. Wilcox, attn: O. L. Burchett
J. R. Craig
A. C. Schwarz

2515	M. L. Lieberman		(5)
2515	D. L. Marchi		
2515	F. J. Villa		
2516	W. G. Perkins, attn:	R. G. Jungst J. W. Rogers	
2516	V. M. Loyola		
2516	T. M. Massis		
2551	E. A. Kjeldgaard		
4218	J. K. Rice		
4310	C. C. Burks, attn:	D. L. McCoy H. T. Lehman	
4330	H. W. Schmitt, attn:	P. A. Longmire O. M. Fligner W. R. Reynolds T. A. Moshenrose	
5131	B. Morosin		
5510	D. B. Hayes, attn:	J. W. Nunziato D. W. Larson	
5820	R. E. Whan, attn:	N. E. Brown R. M. Merrill K. H. Eckelmeyer E. J. Graeber D. H. Huskisson	
8162	A. S. Rivenes		
3141	T. L. Werner		(5)
3151	W. L. Garner for DOE/TIC		(3)
3154-3	R. P. Campbell for DOE/TIC		(25)

[redacted] [redacted]

Org.	Bldg.	Name	Rec'd by *	Org.	Bldg.	Name	Rec'd by *

* Recipient must initial on classified documents.