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THE PHENOMENOLOGY OF SYNERGISTIC
CATALYZED PROPELLANTS

SECOND SEMI-ANNUAL TECHNICAL REPORT
1 NOVEMBER 1970 THROUGH 30 APRIL 1971

ONR CONTRACT N00014-70-C-0554



Rockaldyne
North American Rockwell

SOLID ROCKET DIVISION
P.O. Box 500
McGuire, Texas 78857

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Prepared by

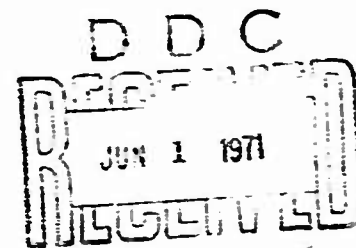
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13. ABSTRACT Report covers the second 6 months of a continuing study of the Keenan catalyst system that consists of a transition metal and a chloride. Initial DSC experiments produced some results that contradicted those of Keenan, but micro DTA experiments tended to confirm his results. DTA work was confined to isothermal work with glass-covered thermocouples. The TGA was used primarily in the isothermal mode at several temperatures to study the relative rates of decomposition. The DSC was used to study the AP catalyzed system, both as oxidizer/catalyst samples and as micromix propellant samples. Data from 11 batches of ammonium nitrate extrudable propellants are presented, and methods by which they were obtained are described. Computer print-outs of a least squares fit of strand burning rate data are included. Strand burning rates continue to verify burning rate depression by chloride. Results obtained to date from this study support the theory that suppression of the burning rate of ammonium dichromate catalyzed propellants occurs in the condensed phase. Isothermal TGA showed no induction time with the synergistic decomposition catalyst and a relatively constant rate of decomposition at each temperature studied. It appears that the induction time observed by Keenan was actually a self-heating time, and it is likely that the nitrogen sparge that Keenan used to delay the induction time was actually only carrying heat away from the sample convectively so that the sample did not reach a high enough temperature to decompose rapidly. DSC and DTA work with micro samples have led to the conclusion that most of the heat release in the sample is in the gas phase and not the condensed phase.		

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Ammonium Nitrate Propellants Differential Scanning Calorimeter Thermogravimetric Analyzer Thermogram Differential Thermal Analyzer Ammonium Chloride Ammonium Perchlorate Propellants Ammonium Dichromate						

INTRODUCTION

This report covers the second 6 months of a continuing study of the Keenan catalyst system. This catalyst consists of a transition metal and a chloride, which A. G. Keenan found to be synergistic for the catalysis of ammonium nitrate decomposition.¹ Initial DSC experiments produced some results that contradicted those of Keenan; however, micro DTA experiments tended to confirm his results.

Extensive use of the TGA during this reporting period resulted in a clearer understanding of the phenomenology of this catalyst system. The use of the TGA has also afforded an explanation of the difference between DSC and DTA results. Eleven propellant mixes were made, and burning rate data were obtained over a relatively wide pressure range. As in the previous report only representative thermograms are included.

EXPERIMENTAL APPROACH

The experimental approach has been continued essentially as described in the first 6-month report.² Work with the DTA was confined to isothermal work with glass-covered thermocouples. The TGA was used primarily in the isothermal mode at a number of different temperatures to study the relative rates of decomposition. The DSC was used to initiate the study of the AP catalyzed system, both as oxidizer/catalyst samples and as micromix propellant samples.

Samples for the ammonium perchlorate study were prepared from the melt samples described in the previous report. Ground melts were mixed with plant-ground AP (approximately 20 microns average particle size)

¹Keenan, A. G.: Mechanism of Reactions of Oxidizer, Contract Nonr-4008(07), May 1966.

²Sammons, G. D.: The Phenomenology of Synergistic Catalyzed Propellants, Semi-annual Technical Report, ONR Contract 00014-70-C-0354, R-4646, November 1970.

in a wig-1-bug mixer. Table 1 shows the composition of these mixtures. DSC thermograms for each sample are presented in Fig. 1 through 8.

TABLE 1
AP SAMPLE COMPOSITIONS

Sample Number	Weight Fraction*					Melt Number
	AN	AC	SC	AD	PD	
4B-12-16	0.1000					9A
5B-12-16	0.0998			0.0002		3B
6B-12-16	0.0967	0.0033				11A
7B-12-16	0.0998				0.0002	13A
8B-12-16	0.0965		0.0035			10A
9B-12-16	0.0962		0.0035		0.0002	14A
10B-12-16	0.0965	0.0033		0.0002		2B

* All samples contain 0.9 weight fraction of 20 micron AP

LEGEND: AN = ammonium nitrate
 AP = ammonium perchlorate
 AC = ammonium chloride
 SC = sodium chloride
 AD = ammonium dichromate
 PD = potassium dichromate

Seven of the 11 batches of propellant were ammonium nitrate extrudable propellants mixed in a 0.7-gallon horizontal Baker-Perkins mixer. The other batches were castable ammonium perchlorate propellants mixed in a 1-pint vertical Baker-Perkins mixer. Strands of the nitrate propellant about 3/16 inch in diameter were extruded and cured at 88 degrees for 48 hours for burning rate studies. A short section of 0.5-inch rod was extruded, cured, cut into 1-inch lengths, and sliced on a microtome. Samples for the DSC were prepared by punching a disc with a No. 1 cork borer from a microtome slice about 0.25 millimeter thick. Strands of the castable perchlorate propellant were prepared by extruding the fluid uncured propellant into restrictor-coated drinking straws. The extruded nitrate strands were coated with methyl methacrylate before they were burned.

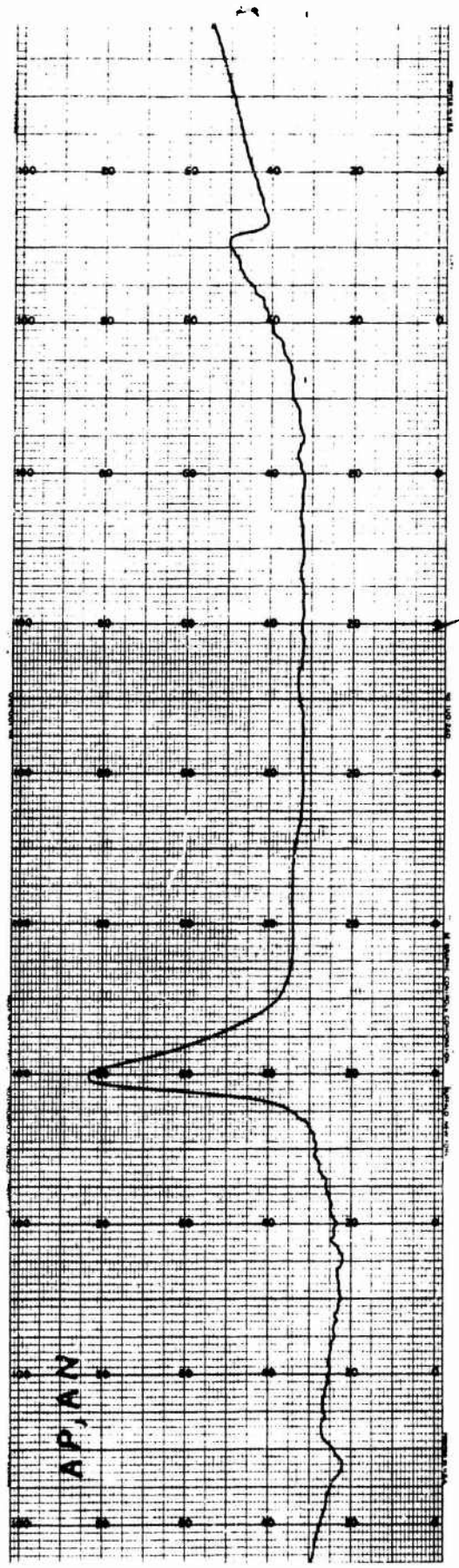


Figure 1. DSC Thermogram of AP Sample 4B-12-16 at 20 deg/min (Sample Weight 3.00 milligrams)

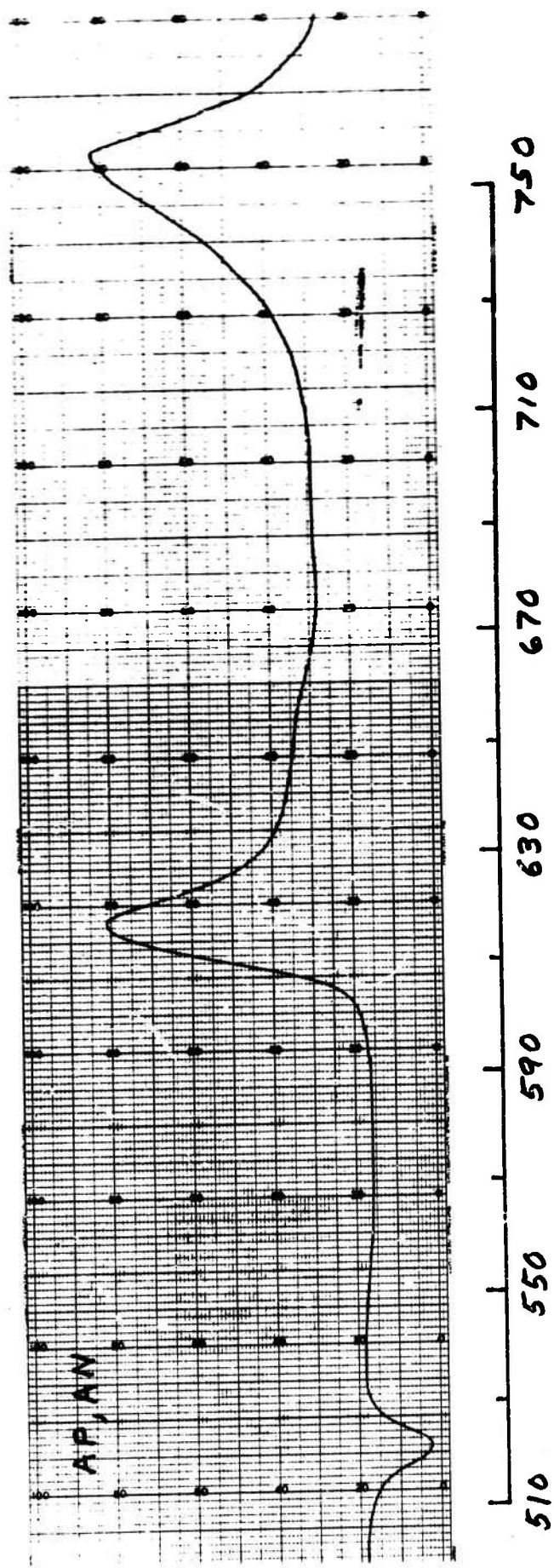


Figure 2. DSC Thermogram of AP Sample 4B-12-16 at 80 deg/min (Sample weight 3.00 milligrams)

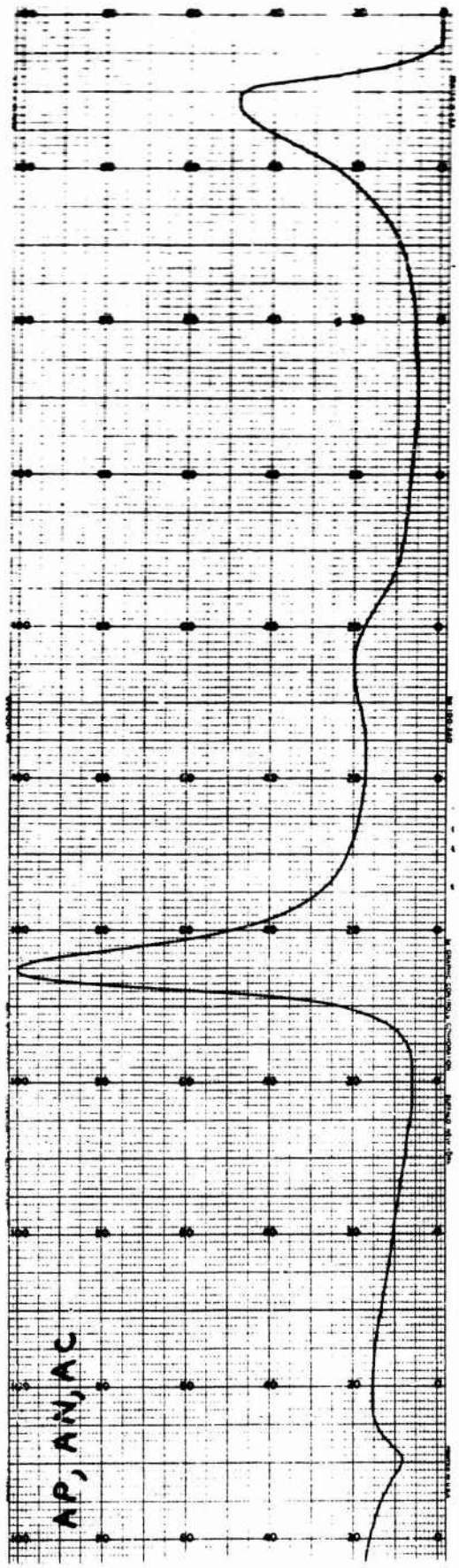


Figure 3. DSC Thermogram of AP Sample 6B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

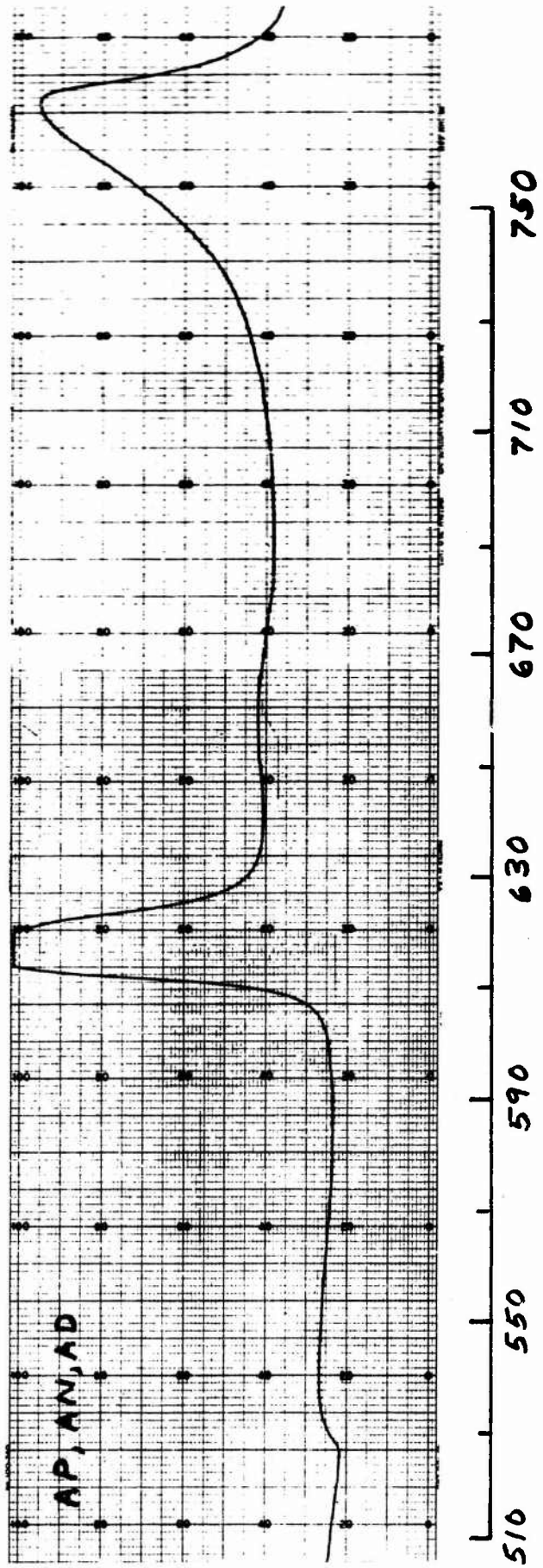


Figure 4. DSC Thermogram of AP Sample 5B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

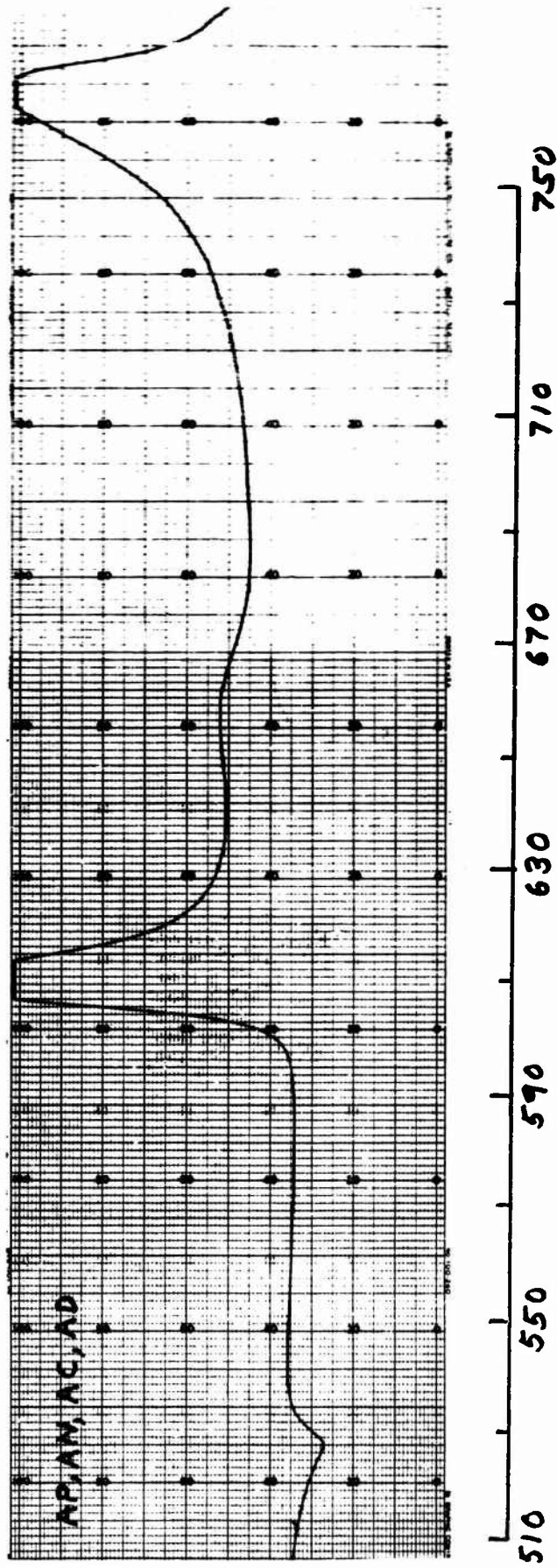
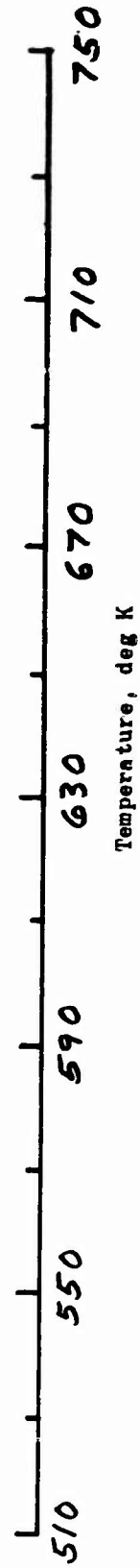
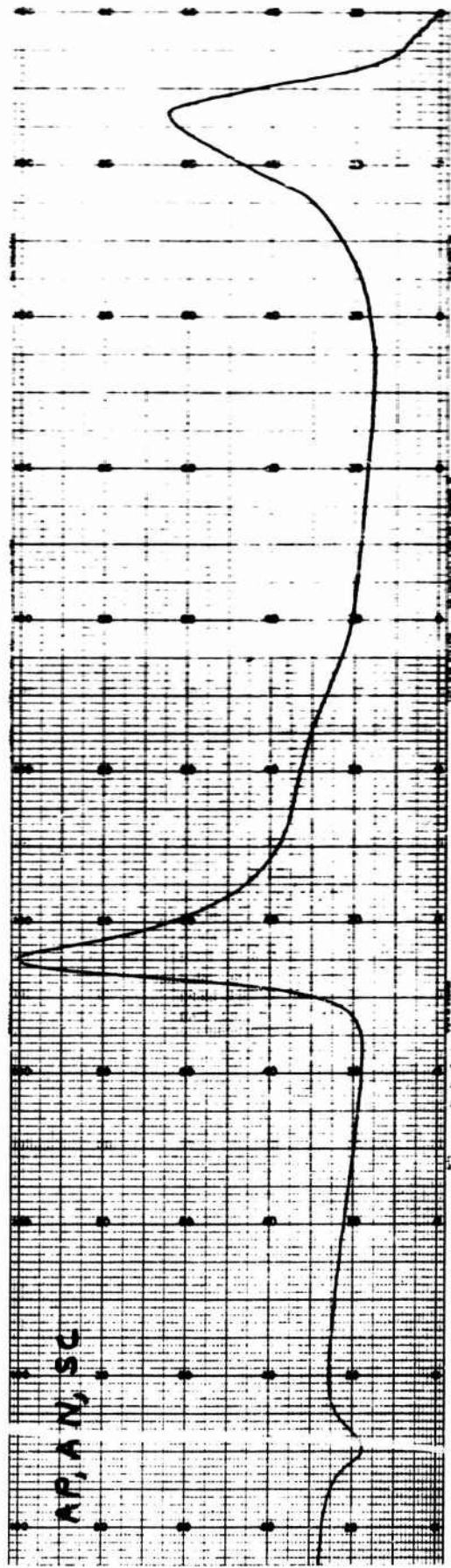


Figure 5. DSC Thermogram of AP Sample 10B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)



Temperature, deg K

∞ Figure 6. DSC Thermogram of AP Sample 8B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

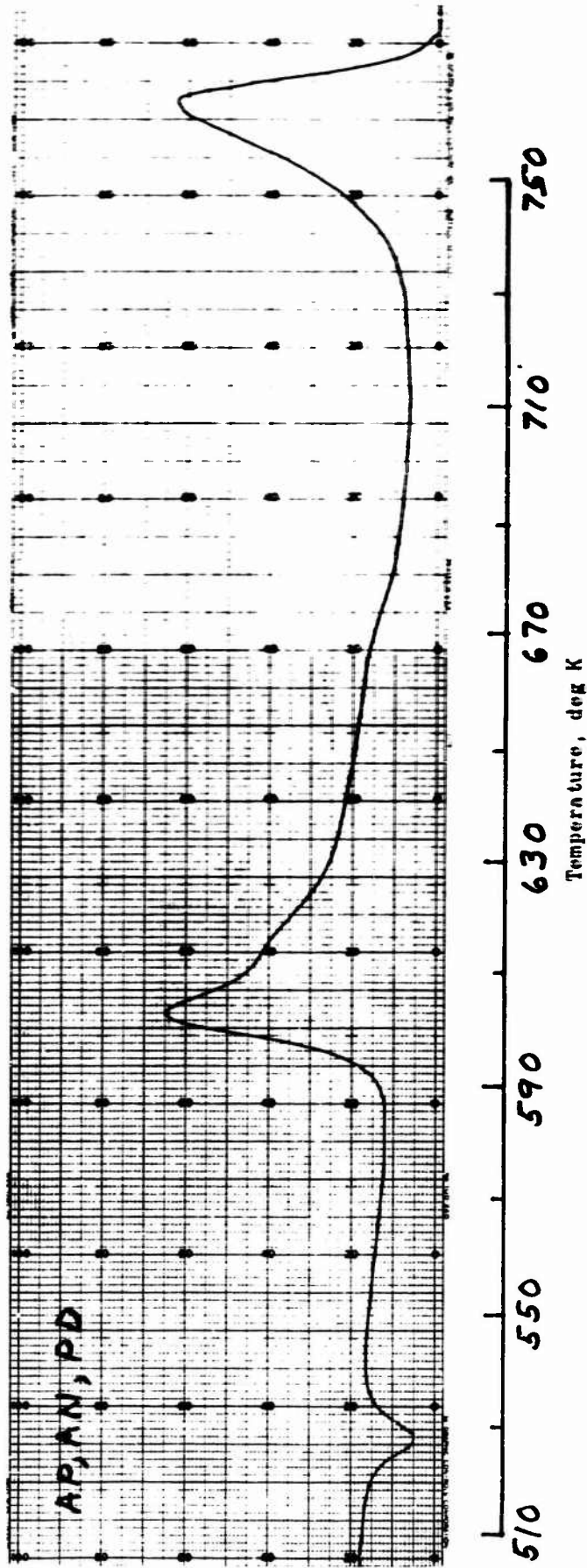


Figure 7. DSC Thermogram of AP Sample 7B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

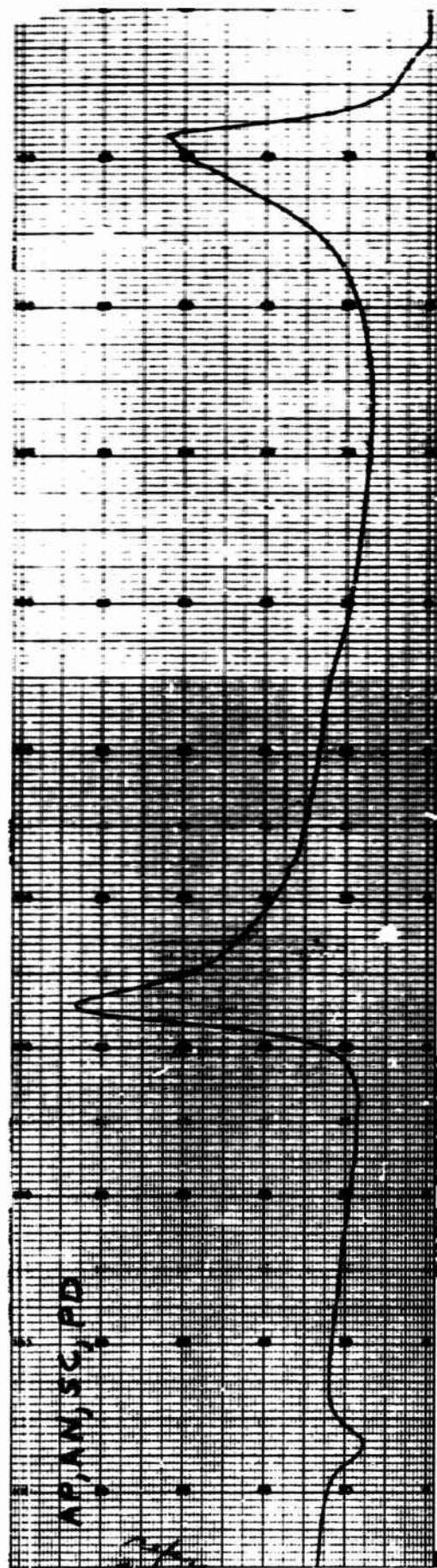


Figure 8. DSC Thermogram of AP Sample 9B-12-16 at 80 deg/min (Sample Weight 3.00 milligrams)

All strands were burned in 3-inch lengths in a standard Crawford bomb. Four replicates were burned at each of 200, 300, 500, 800, 1000, 1200, and 1500 psi nitrogen pressure.

ISOTHERMAL DTA

The duPont model 900 DTA was used in this study. All of the thermograms were run isothermally during this period and were made with thermocouples thinly coated with Pyrex glass.

The results obtained were surprising because in no case was an exotherm observed. Samples of about 20 milligrams were held at a number of temperatures from 195 to 250 C until the sample was completely decomposed. At present this can only be attributed to the difference in heat transfer due to the micro samples. Again, it appears that in the presence of the chloride, most of the exotherm is in the gas phase, as previously observed in dynamic runs.

DYNAMIC DSC (AP CATALYSIS)

Thermograms were run at 20 and 80 deg/min since it was found in previous studies that no reliable interpretations could be made without data from at least two scan rates. Comparison of Fig. 1 and 2 reveals that most information could be gained from the thermogram taken at 80 deg/min when AN/AP mixtures are being studied; apparently the presence of AN accelerates the sublimation of AP and almost all of the sample is gone before the high-temperature decomposition exotherm is reached.

Comparison of Fig. 2 and 3 shows very significant catalysis by ammonium chloride. Comparison of Fig. 4 and 7 indicates a better catalysis by ammonium dichromate than by potassium dichromate. This last assessment is based on the AP crystal phase change shown in the two figures; apparently ammonium dichromate lowered the activation energy more than the potassium salt. The near absence of an AP crystal phase

change in Fig. 4 is a sensitive indicator of an early exotherm, which means a low activation energy. This represents a good correlation with ballistic data since ammonium dichromate is known to be the best burn rate catalyst.

The special "Micromix" technique described in the last report was used to study the activity of the samples described in Table 1 in the presence of fuel. These samples have only been run at 20 deg/min thus far. Surprisingly, all of these micropropellants ignited at this heating rate. Based on the part of the curve obtained before ignition and the point of ignition, ammonium dichromate was again shown to be more effective than potassium dichromate (see Fig. 12 and 13). Sodium chloride and ammonium chloride again appeared to suppress the effect of chromium (see Fig. 9 to 13).

ISOTHERMAL TGA

A considerable number of isothermal thermogravimetric analyses were made in an effort to understand more fully the nature of the decomposition catalyst system being studied. These TGA thermograms were run as described in the last report with less than 3 minutes to equilibrium at the desired temperature. The upper curve in the example thermograms (Fig. 14 to 17) is a record of sample weight during the heat-up period and has temperature as the abscissa. When the desired temperature was reached the program was switched to isothermal and time base with 5 minutes per inch scale (30 seconds per small division). The distance from the zero abscissa to the start of the time base record indicates the time elapsed during heat-up. The encircled data represent temperature checks during the run.

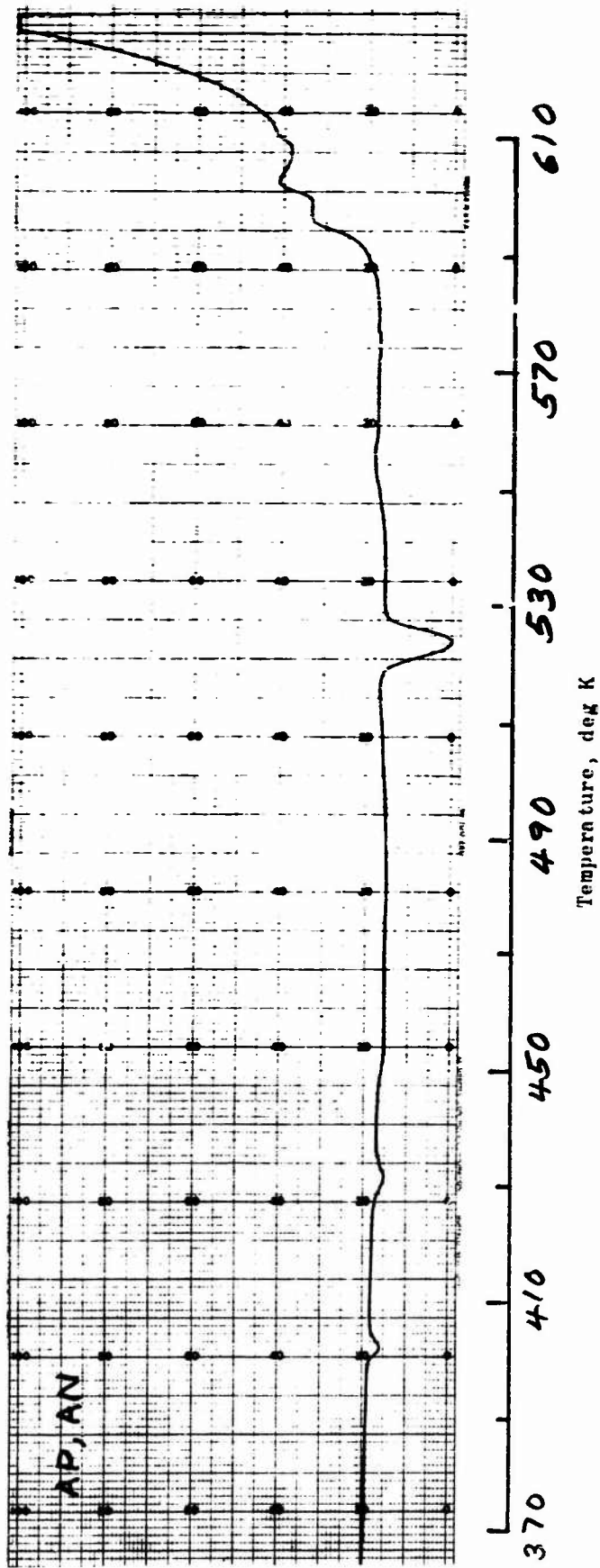


Figure 9. DSC Thermogram of Micromix Propellant of AP Sample 4B-12-16 at 20 deg/min
(Sample Weight 3.00 milligrams plus 0.70 milligram Binder)

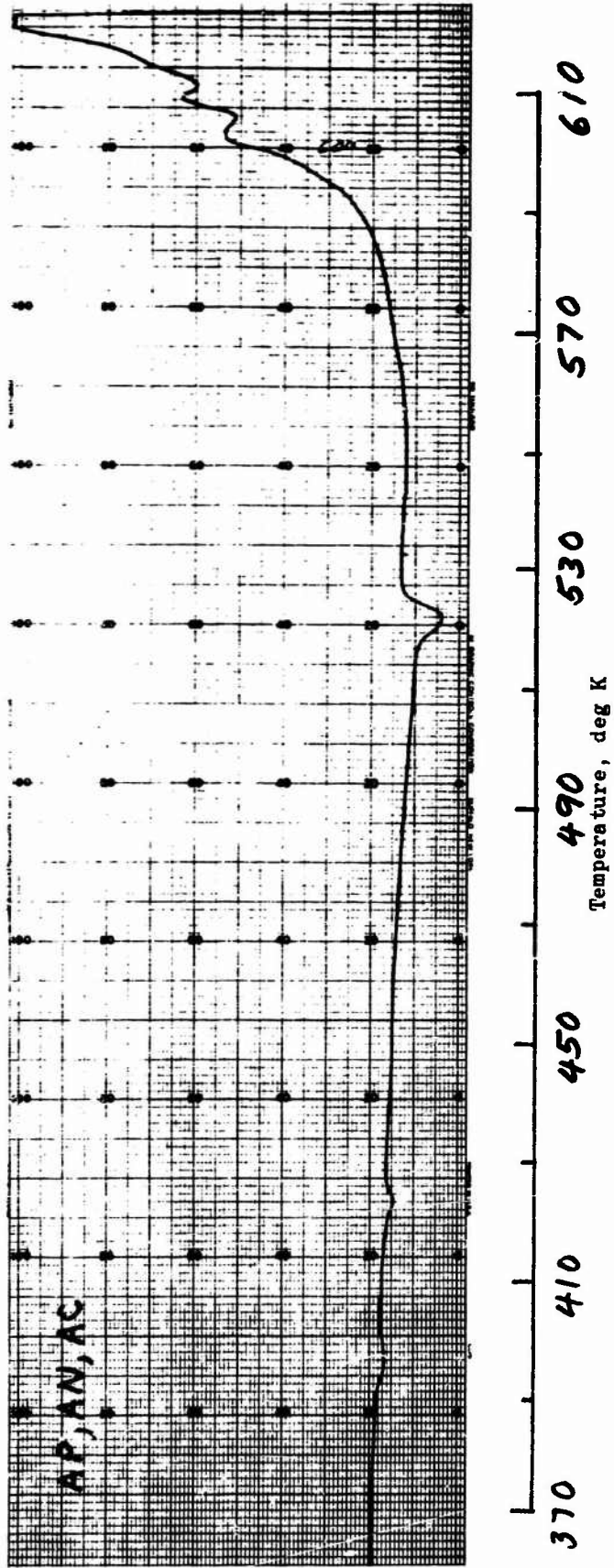


Figure 10. DSC Thermogram of Micromix Propellant of AP Sample 6B-12-16 at 20 deg/min
 (Sample Weight 3.00 milligrams Plus 0.59 milligram Binder)

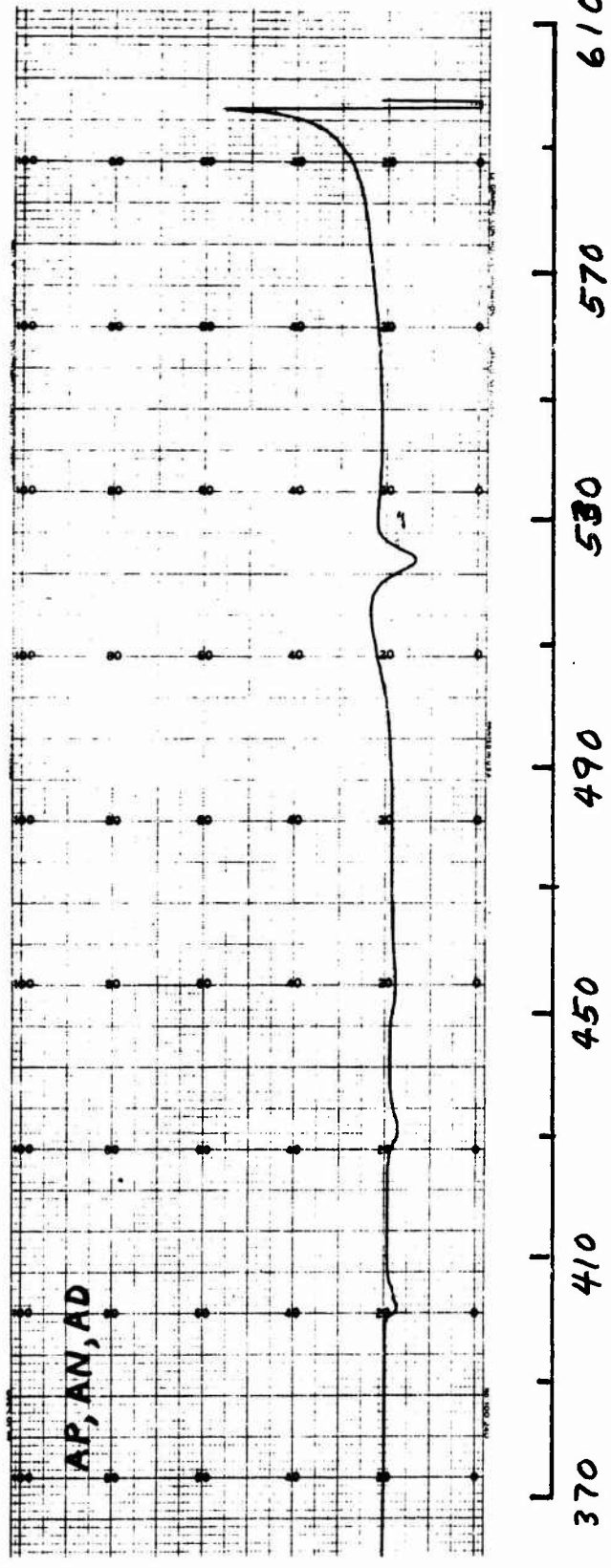


Figure 11. DSC Thermogram of Micromix Propellant of AP Sample 5B-12-16 at 20 deg/min
 (Sample Weight 3.00 milligrams Plus 0.62 milligram Binder)

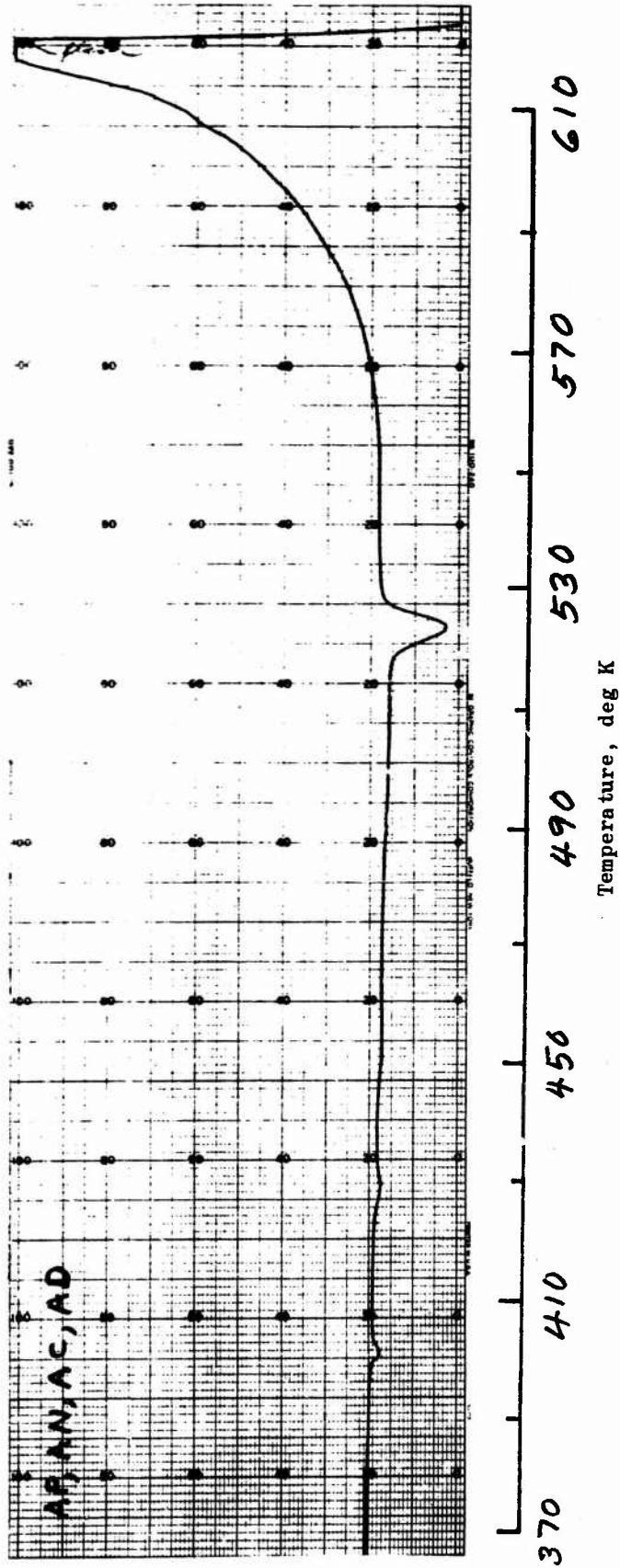
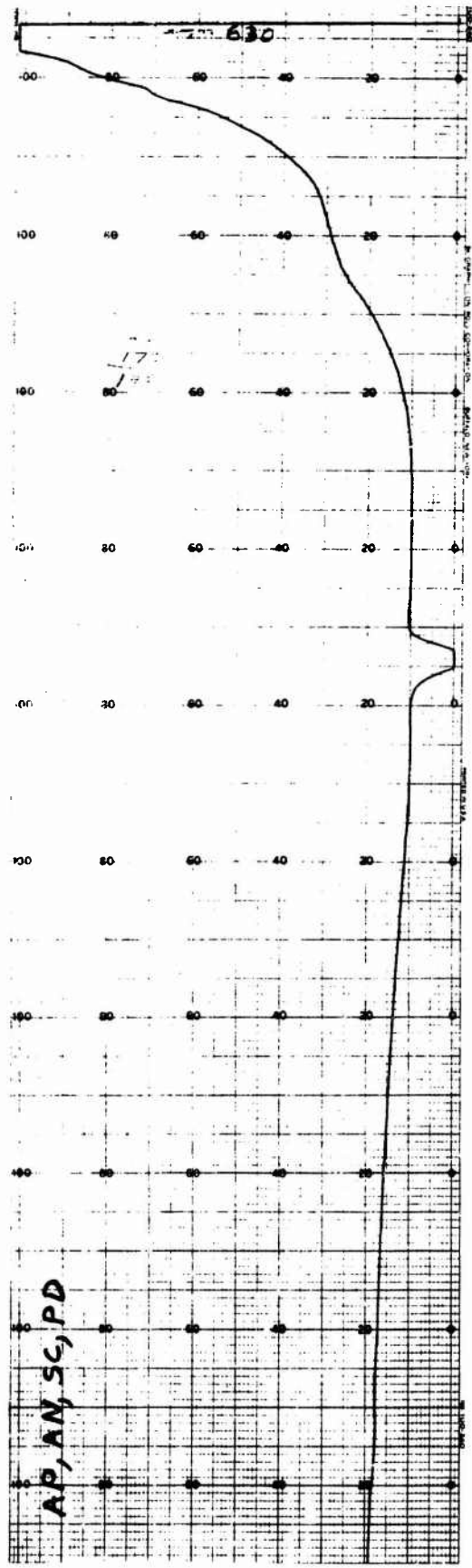
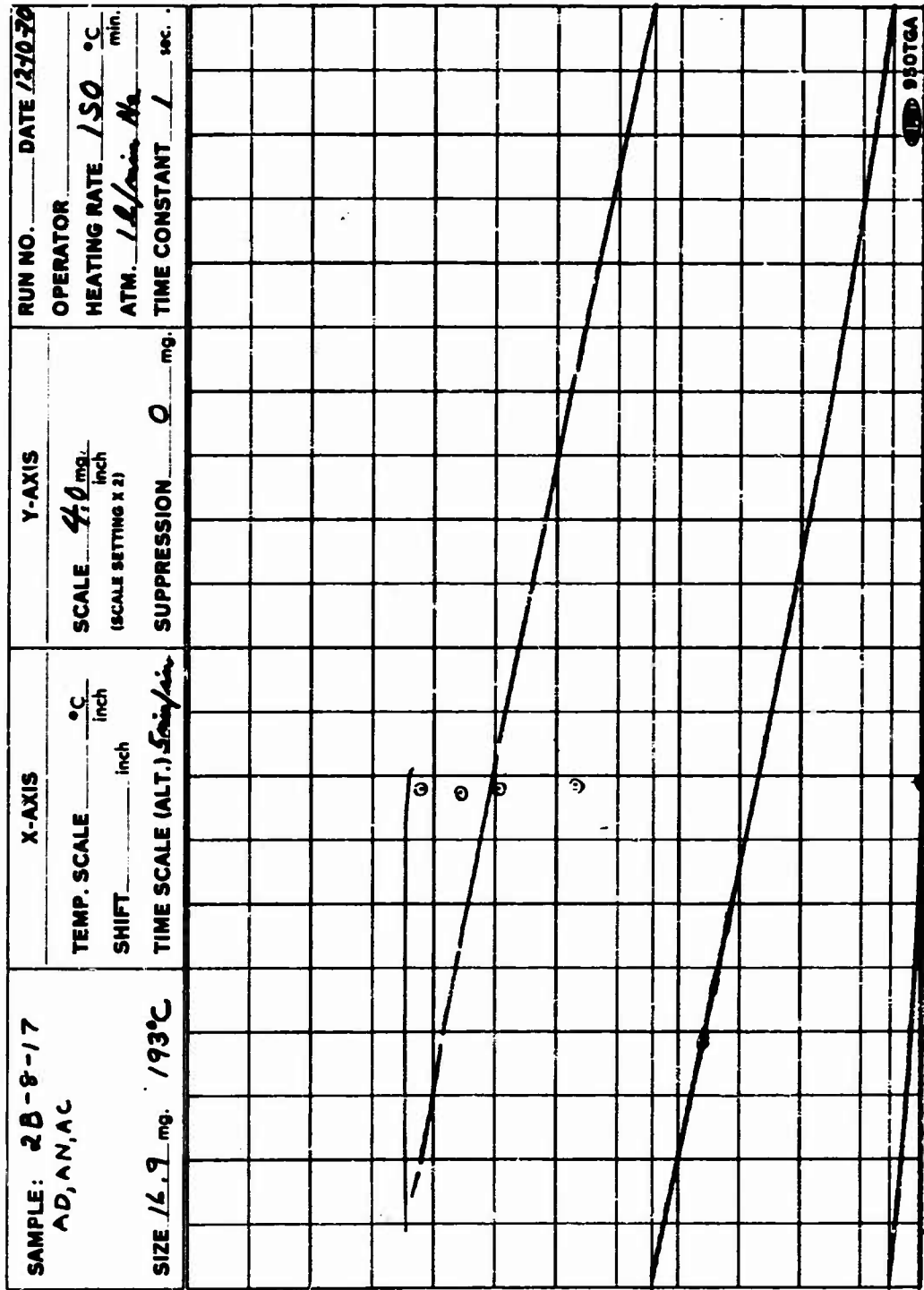


Figure 12. DSC Thermogram of Micromix Propellant of AP Sample 10B-12-16 at 20 deg/min (Sample Weight 3.00 milligrams Plus 1.12 milligrams Binder)



370 410 450 490 530 570 610
 Temperature, deg K

Figure 13. DSC Thermogram of Micromix Propellant of AP Sample 9B-12-16 at 20 deg/min
 (Sample Weight 3.00 milligrams Plus 0.58 milligram Binder)



* APPLY CORRECTIONS FOR NONLINEARITY OF CALIBRATION VALUES TEMPERATURES

Figure 14. Isothermal TGA of Mix Sample 2B-8-17 at 193 C

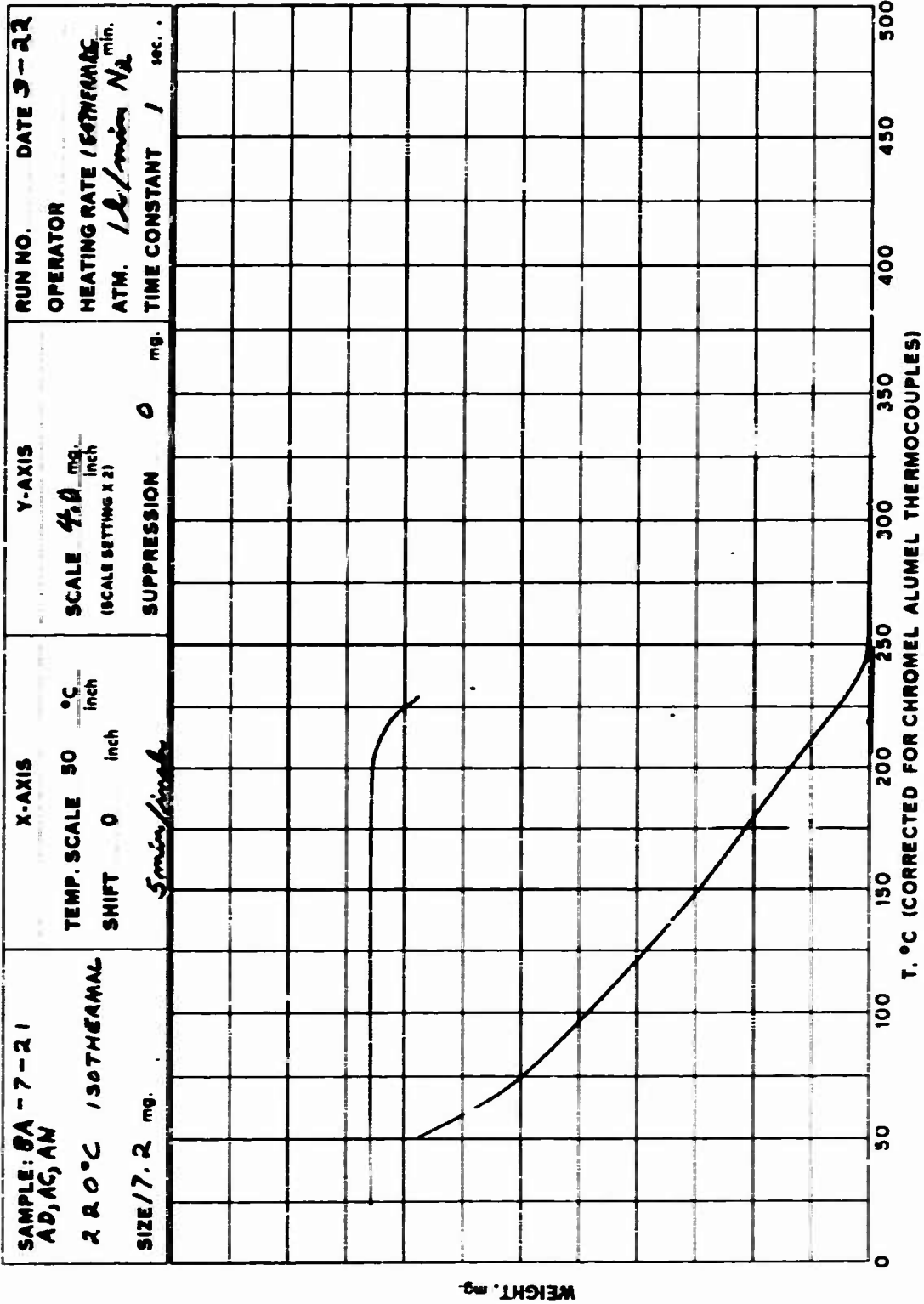


Figure 15. Isothermal TGA of Mix Sample BA-7-22 at 220 C

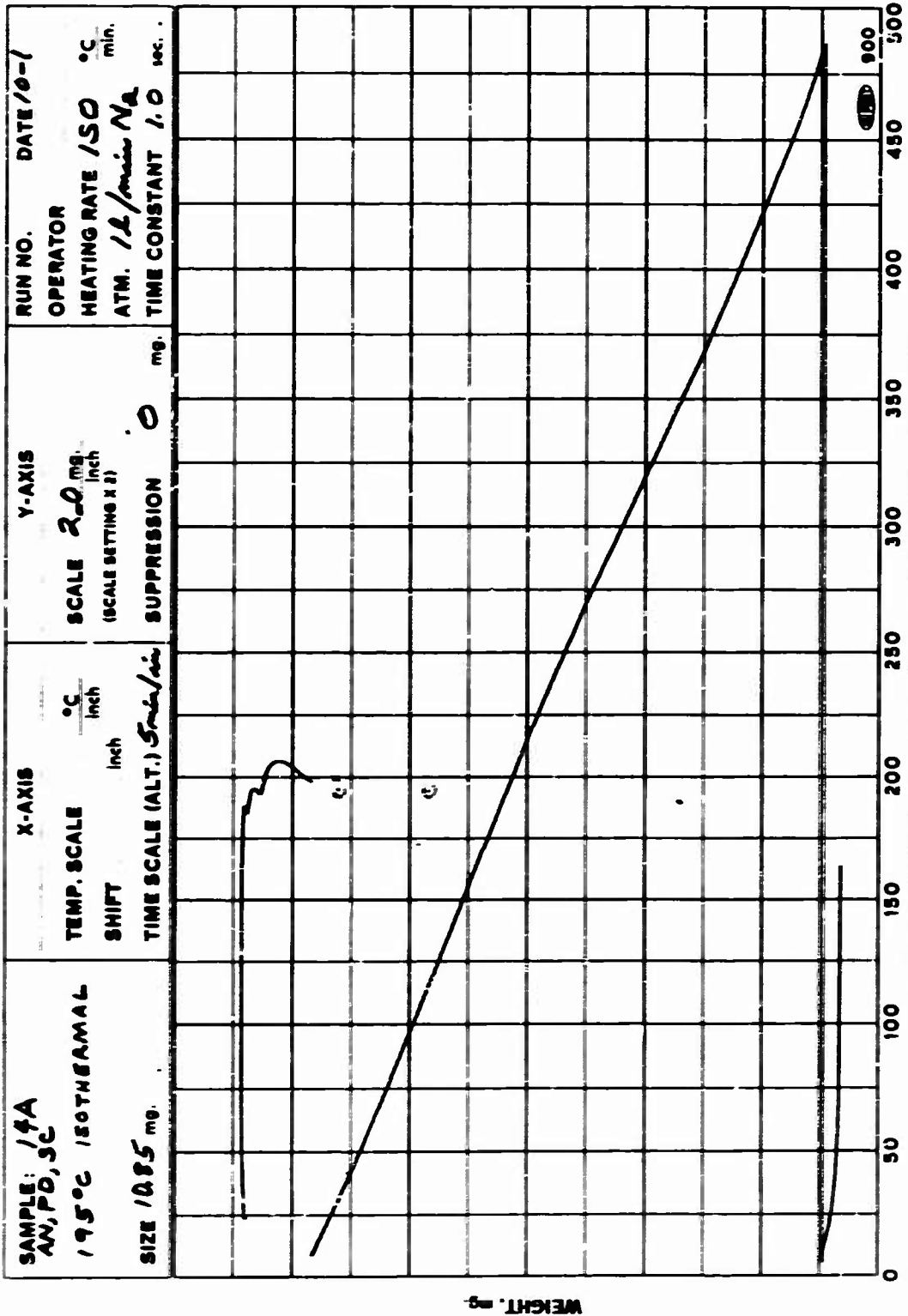


Figure 16. Isothermal TGA of Mix Sample 14A-7-30 at 195 C

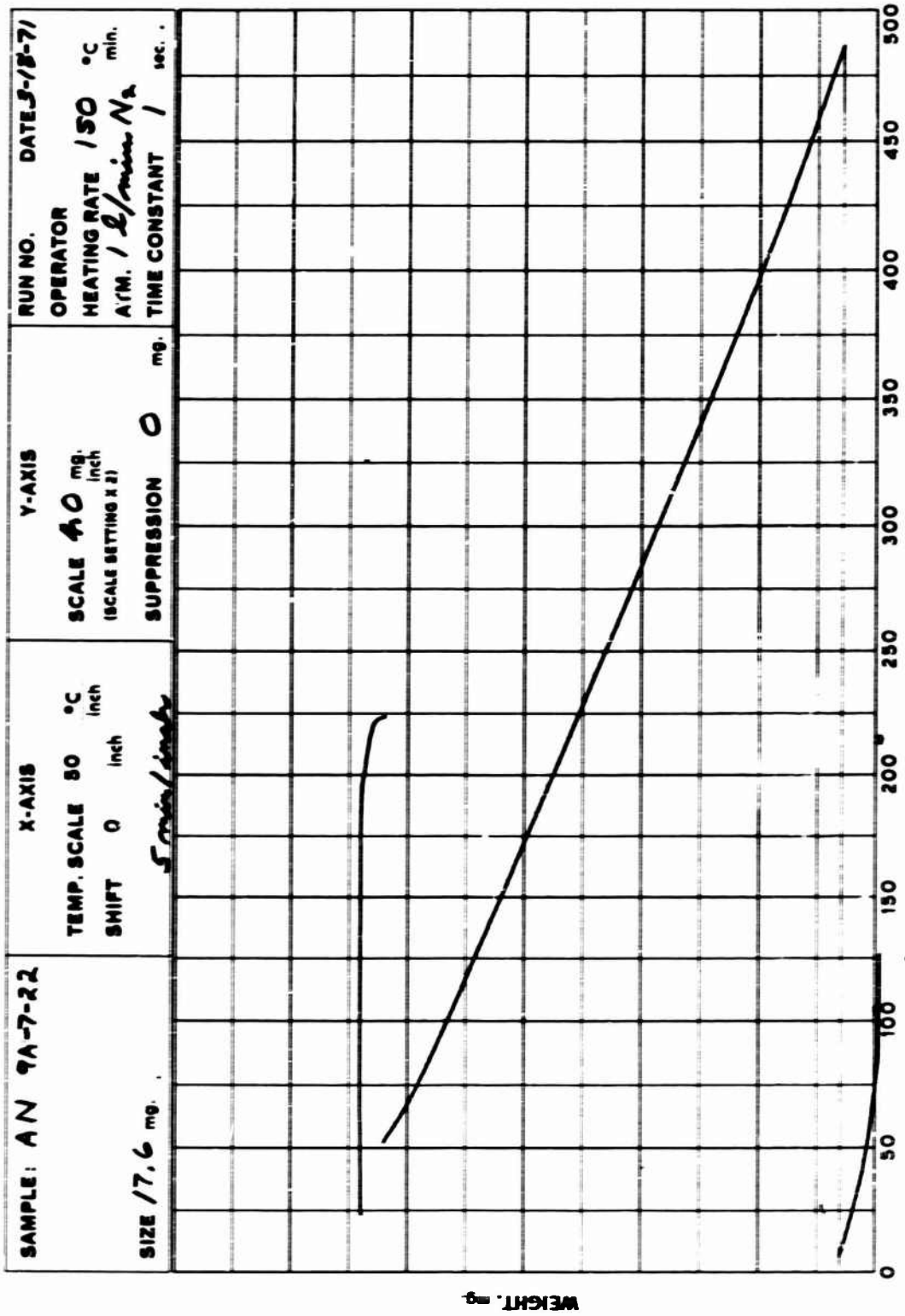


Figure 17. Isothermal TGA of Ammonium Nitrate Sample 9A-7-22 at 213 C

Keenan observed an induction time of over 60 minutes with the chromium/chloride catalyst system at 195 C furnace temperature. As shown in Fig. 15, no induction time was observed by TGA at 195 C; and, in fact, none was observed at any temperature above 195 C. In Fig. 15 decomposition started just before the sample reached 195 C and according to the time base recording the sample decomposed at an almost constant rate until it was totally consumed.

The rate constant of decomposition was obtained by calculating the slope of $\ln(\text{weight})$ vs time. This gives a quantitative parameter for comparison purposes. Table 2 contains this data reduced from some of the isothermal runs. No attempt was made to least squares fit data or determine reaction order since kinetic parameters were not of particular interest in this program. First order kinetics were assumed so that a comparative parameter could be obtained easily.

TABLE 2
EFFECTIVE RATE CONSTANTS BY THERMOGRAVIMETRIC
ANALYSIS FOR ISOTHERMAL DECOMPOSITIONS

Sample Number	Temperature, deg C	Rate Constant $\times 10^2$, min ⁻¹
14A-7-30 (AN, PD, SC)	187	1.75
	190	1.98
	195	1.59
	202	10.66
	205	11.71
	217	10.64
	220	12.27
9B-7-22 (AN)	195	2.77
	202	3.14
	218	3.96
11A-7-22 (AN, AC)	220	5.03
10A-7-22 (AN, SC)	214	4.86
8A-7-21 (AN, AD, AC)	218	6.75
2B-8-17 (AN, AD, AC)	193	2.18
Co-Crystallized (0.17% Cl)	195	2.38
	218	4.80
Co-Crystallized (12.0% Cl)	216	4.30

Table 2 indicates that a number of runs should be made to verify some of the values and clarify some of the trends. The most informative trends are given by sample 14A (AN, PD, SC) and 9B (AN). The effectiveness of the catalyst system with alkali metal salts is very pronounced. A significant increase in rate occurs around 200 C.

Sample 8A indicates the ammonium salts may be less effective as a decomposition catalyst than the alkali metal salts. More runs should be made with the AP salts. Comparing 11A and 10A with 9B (AN alone) indicates catalysis by sodium or ammonium chloride of about the same degree.

PROPELLANT MIXES (AMMONIUM NITRATE)

The composition of the seven batches of AN propellants made during this reporting period are listed in Table 3.

TABLE 3
COMPOSITION OF EXTRUDABLE AMMONIUM NITRATE PROPELLANTS

Propellant	Ingredients	Wt %	Actual Weight Used, grams
Control 1A	Binder	19.44	194.40
	Magnesium Oxide	0.54	5.40
	Ammonium Nitrate	79.86	798.60
	Ammonium Dichromate	0.16	1.60
			<u>1000.00</u>
Catalyzed 3	Binder	18.87	188.70
	Magnesium Oxide	0.52	5.20
	Ammonium Nitrate	77.51	775.10
	Ammonium Dichromate	0.58	5.80
	Sodium Chloride	2.52	25.20
			<u>1000.00</u>
Catalyzed 4	Binder	18.87	188.70
	Magnesium Oxide	0.52	5.20
	Ammonium Nitrate	77.51	775.10
	Ammonium Dichromate	0.58	5.80
	Ammonium Chloride	2.52	25.20
			<u>1000.00</u>
Control 5*	Binder	20.00	200.00
	Ammonium Nitrate	79.50	795.00
	Ammonium Dichromate	0.50	5.00
			<u>1000.00</u>
Catalyzed 5	Binder	19.47	194.70
	Ammonium Nitrate	77.41	774.10
	Ammonium Dichromate	0.49	4.90
	Ammonium Chloride	2.63	26.30
			<u>1000.00</u>

* Control and catalyzed propellants were made twice. The first mix did not process satisfactorily.

Tables 4 through 8 are computer print-outs of a least squares fit of strand burn rate data. The data point at each pressure represents a simple average of at least four tests. Reduced data are plotted in Fig. 18 through 20.

TABLE 4
LEAST SQUARES FIT OF BURNING RATE DATA
ON PROPELLANT CONTROL 1A

0.0000
YOUR VALUE FOR REFERENCE PRESSURE IS 21000
YOUR VALUES OF PRESSURE AND RATE ARE 2100, .017
2200, .025
2300, .033
2400, .041
2500, .049
2600, .057
2700, .065
2800, .073
2900, .081
3000, .089
3100, .097
3200, .105
3300, .113
3400, .121
3500, .129
3600, .137
3700, .145
3800, .153
3900, .161
4000, .169
4100, .177
4200, .185
4300, .193
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4500, .209
4600, .217
4700, .225
4800, .233
4900, .241
5000, .249
5100, .257
5200, .265
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5600, .297
5700, .305
5800, .313
5900, .321
6000, .329
6100, .337
6200, .345
6300, .353
6400, .361
6500, .369
6600, .377
6700, .385
6800, .393
6900, .401
7000, .409
7100, .417
7200, .425
7300, .433
7400, .441
7500, .449
7600, .457
7700, .465
7800, .473
7900, .481
8000, .489
8100, .497
8200, .505
8300, .513
8400, .521
8500, .529
8600, .537
8700, .545
8800, .553
8900, .561
9000, .569
9100, .577
9200, .585
9300, .593
9400, .601
9500, .609
9600, .617
9700, .625
9800, .633
9900, .641
10000, .649
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10300, .673
10400, .681
10500, .689
10600, .697
10700, .705
10800, .713
10900, .721
11000, .729
11100, .737
11200, .745
11300, .753
11400, .761
11500, .769
11600, .777
11700, .785
11800, .793
11900, .801
12000, .809
12100, .817
12200, .825
12300, .833
12400, .841
12500, .849
12600, .857
12700, .865
12800, .873
12900, .881
13000, .889
13100, .897
13200, .905
13300, .913
13400, .921
13500, .929
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13700, .945
13800, .953
13900, .961
14000, .969
14100, .977
14200, .985
14300, .993
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14500, 1.009
14600, 1.017
14700, 1.025
14800, 1.033
14900, 1.041
15000, 1.049
15100, 1.057
15200, 1.065
15300, 1.073
15400, 1.081
15500, 1.089
15600, 1.097
15700, 1.105
15800, 1.113
15900, 1.121
16000, 1.129
16100, 1.137
16200, 1.145
16300, 1.153
16400, 1.161
16500, 1.169
16600, 1.177
16700, 1.185
16800, 1.193
16900, 1.201
17000, 1.209
17100, 1.217
17200, 1.225
17300, 1.233
17400, 1.241
17500, 1.249
17600, 1.257
17700, 1.265
17800, 1.273
17900, 1.281
18000, 1.289
18100, 1.297
18200, 1.305
18300, 1.313
18400, 1.321
18500, 1.329
18600, 1.337
18700, 1.345
18800, 1.353
18900, 1.361
19000, 1.369
19100, 1.377
19200, 1.385
19300, 1.393
19400, 1.401
19500, 1.409
19600, 1.417
19700, 1.425
19800, 1.433
19900, 1.441
20000, 1.449
20100, 1.457
20200, 1.465
20300, 1.473
20400, 1.481
20500, 1.489
20600, 1.497
20700, 1.505
20800, 1.513
20900, 1.521
21000, 1.529
21100, 1.537
21200, 1.545
21300, 1.553
21400, 1.561
21500, 1.569
21600, 1.577
21700, 1.585
21800, 1.593
21900, 1.601
22000, 1.609
22100, 1.617
22200, 1.625
22300, 1.633
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22500, 1.649
22600, 1.657
22700, 1.665
22800, 1.673
22900, 1.681
23000, 1.689
23100, 1.697
23200, 1.705
23300, 1.713
23400, 1.721
23500, 1.729
23600, 1.737
23700, 1.745
23800, 1.753
23900, 1.761
24000, 1.769
24100, 1.777
24200, 1.785
24300, 1.793
24400, 1.801
24500, 1.809
24600, 1.817
24700, 1.825
24800, 1.833
24900, 1.841
25000, 1.849
25100, 1.857
25200, 1.865
25300, 1.873
25400, 1.881
25500, 1.889
25600, 1.897
25700, 1.905
25800, 1.913
25900, 1.921
26000, 1.929
26100, 1.937
26200, 1.945
26300, 1.953
26400, 1.961
26500, 1.969
26600, 1.977
26700, 1.985
26800, 1.993
26900, 2.001
27000, 2.009
27100, 2.017
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27300, 2.033
27400, 2.041
27500, 2.049
27600, 2.057
27700, 2.065
27800, 2.073
27900, 2.081
28000, 2.089
28100, 2.097
28200, 2.105
28300, 2.113
28400, 2.121
28500, 2.129
28600, 2.137
28700, 2.145
28800, 2.153
28900, 2.161
29000, 2.169
29100, 2.177
29200, 2.185
29300, 2.193
29400, 2.201
29500, 2.209
29600, 2.217
29700, 2.225
29800, 2.233
29900, 2.241
30000, 2.249
30100, 2.257
30200, 2.265
30300, 2.273
30400, 2.281
30500, 2.289
30600, 2.297
30700, 2.305
30800, 2.313
30900, 2.321
31000, 2.329
31100, 2.337
31200, 2.345
31300, 2.353
31400, 2.361
31500, 2.369
31600, 2.377
31700, 2.385
31800, 2.393
31900, 2.401
32000, 2.409
32100, 2.417
32200, 2.425
32300, 2.433
32400, 2.441
32500, 2.449
32600, 2.457
32700, 2.465
32800, 2.473
32900, 2.481
33000, 2.489
33100, 2.497
33200, 2.505
33300, 2.513
33400, 2.521
33500, 2.529
33600, 2.537
33700, 2.545
33800, 2.553
33900, 2.561
34000, 2.569
34100, 2.577
34200, 2.585
34300, 2.593
34400, 2.601
34500, 2.609
34600, 2.617
34700, 2.625
34800, 2.633
34900, 2.641
35000, 2.649
35100, 2.657
35200, 2.665
35300, 2.673
35400, 2.681
35500, 2.689
35600, 2.697
35700, 2.705
35800, 2.713
35900, 2.721
36000, 2.729
36100, 2.737
36200, 2.745
36300, 2.753
36400, 2.761
36500, 2.769
36600, 2.777
36700, 2.785
36800, 2.793
36900, 2.801
37000, 2.809
37100, 2.817
37200, 2.825
37300, 2.833
37400, 2.841
37500, 2.849
37600, 2.857
37700, 2.865
37800, 2.873
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38200, 2.905
38300, 2.913
38400, 2.921
38500, 2.929
38600, 2.937
38700, 2.945
38800, 2.953
38900, 2.961
39000, 2.969
39100, 2.977
39200, 2.985
39300, 2.993
39400, 3.001
39500, 3.009
39600, 3.017
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39800, 3.033
39900, 3.041
40000, 3.049
40100, 3.057
40200, 3.065
40300, 3.073
40400, 3.081
40500, 3.089
40600, 3.097
40700, 3.105
40800, 3.113
40900, 3.121
41000, 3.129
41100, 3.137
41200, 3.145
41300, 3.153
41400, 3.161
41500, 3.169
41600, 3.177
41700, 3.185
41800, 3.193
41900, 3.201
42000, 3.209
42100, 3.217
42200, 3.225
42300, 3.233
42400, 3.241
42500, 3.249
42600, 3.257
42700, 3.265
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44300, 3.393
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44800, 3.433
44900, 3.441
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45100, 3.457
45200, 3.465
45300, 3.473
45400, 3.481
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45600, 3.497
45700, 3.505
45800, 3.513
45900, 3.521
46000, 3.529
46100, 3.537
46200, 3.545
46300, 3.553
46400, 3.561
46500, 3.569
46600, 3.577
46700, 3.585
46800, 3.593
46900, 3.601
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47100, 3.617
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47700, 3.665
47800, 3.673
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48000, 3.689
48100, 3.697
48200, 3.705
48300, 3.713
48400, 3.721
48500, 3.729
48600, 3.737
48700, 3.745
48800, 3.753
48900, 3.761
49000, 3.769
49100, 3.777
49200, 3.785
49300, 3.793
49400, 3.801
49500, 3.809
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51300, 3.953
51400, 3.961
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51600, 3.977
51700, 3.985
51800, 3.993
51900, 4.001
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52200, 4.025
52300, 4.033
52400, 4.041
52500, 4.049
52600, 4.057
52700, 4.065
52800, 4.073
52900, 4.081
53000, 4.089
53100, 4.097
53200, 4.105
53300, 4.113
53400, 4.121
53500, 4.129
53600, 4.137
53700, 4.145
53800, 4.153
53900, 4.161
54000, 4.169
54100, 4.177
54200, 4.185
54300, 4.193
54400, 4.201
54500, 4.209
54600, 4.217
54700, 4.225
54800, 4.233
54900, 4.241
55000, 4.249
55100, 4.257
55200, 4.265
55300, 4.273
55400, 4.281
55500, 4.289
55600, 4.297
55700, 4.305
55800, 4.313
55900, 4.321
56000, 4.329
56100, 4.337
56200, 4.345
56300, 4.353
56400, 4.361
56500, 4.369
56600, 4.377
56700, 4.385
56800, 4.393
56900, 4.401
57000, 4.409
57100, 4.417
57200, 4.425
57300, 4.433
57400, 4.441
57500, 4.449
57600, 4.457
57700, 4.465
57800, 4.473
57900, 4.481
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58600, 4.537
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58800, 4.553
58900, 4.561
59000, 4.569
59100, 4.577
59200, 4.585
59300, 4.593
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60900, 4.721
61000, 4.729
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61400, 4.761
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61600, 4.777
61700, 4.785
61800, 4.793
61900, 4.801
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63700, 4.945
63800, 4.953
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64800, 5.033
64900, 5.041
65000, 5.049
65100, 5.057
65200, 5.065
65300, 5.073
65400, 5.081
65500, 5.089
65600, 5.097
65700, 5.105
65800, 5.113
65900, 5.121
66000, 5.129
66100, 5.137
66200, 5.145
66300, 5.153
66400, 5.161
66500, 5.169
66600, 5.177
66700, 5.185
66800, 5.193
66900, 5.201
67000, 5.209
67100, 5.217
67200, 5.225
67300, 5.233
67400, 5.241
67500, 5.249
67600, 5.257
67700, 5.265
67800, 5.273
67900, 5.281
68000, 5.289
68100, 5.297
68200, 5.305
68300, 5.313
68400, 5.321
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68600, 5.337
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70400, 5.481
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70600, 5.497
70700, 5.505
70800, 5.513
70900, 5.521
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71100, 5.537
71200, 5.545
71300, 5.553
71400, 5.561
71500, 5.569
71600, 5.577
71700, 5.585
71800, 5.593
71900, 5.601
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72700, 5.665
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73500, 5.729
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73700, 5.745
73800, 5.753
73900, 5.761
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74100, 5.777
74200, 5.785
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74400, 5.801
74500, 5.809
74600, 5.817
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74900, 5.841
75000, 5.849
75100, 5.857
75200, 5.865
75300, 5.873
75400, 5.881
75500, 5.889
75600, 5.897
75700, 5.905
75800, 5.913
75900, 5.921
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76100, 5.937
76200, 5.945
76300, 5.953
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76500, 5.969
76600, 5.977
76700, 5.985
76800, 5.993
76900, 6.001
77000, 6.009
77100, 6.017
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77300, 6.033
77400, 6.041
77500, 6.049
77600, 6.057
77700, 6.065
77800, 6.073
77900, 6.081
78000, 6.089
78100, 6.097
78200, 6.105
78300, 6.113
78400, 6.121
78500, 6.129
78600, 6.137
78700, 6.145
78800, 6.153
78900, 6.161
79000, 6.169
79100, 6.177
79200, 6.185
79300, 6.193
79400, 6.201
79500, 6.209
79600, 6.217
79700, 6.225
79800, 6.233
79900, 6.241
80000, 6.249
80100, 6.257
80200, 6.265
80300, 6.273
80400, 6.281
80500, 6.289
80600, 6.297
80700, 6.305
80800, 6.313
80900, 6.321
81000, 6.329
81100, 6.337
81200, 6.345
81300, 6.353
81400, 6.361
81500, 6.369
81600, 6.377
81700, 6.385
81800, 6.393
81900, 6.401
82000, 6.409
82100, 6.417
82200, 6.425
82300, 6.433
82400, 6.441
82500, 6.449
82600, 6.457
82700, 6.465
82800, 6.473
82900, 6.481
83000, 6.489
83100, 6.497
83200, 6.505
83300, 6.513
83400, 6.521
83500, 6.529
83600, 6.537
83700, 6.545
83800, 6.553
83900, 6.561
84000, 6.569
84100, 6.577
84200, 6.585
84300, 6.593
84400, 6.601
84500, 6.609
84600, 6.617
84700, 6.625
84800, 6.633
84900, 6.641
85000, 6.649
85100, 6.657
85200, 6.665
85300, 6.673
85400, 6.681
85500, 6.689
85600, 6.697
85700, 6.705
85800, 6.713
85900, 6.721
86000, 6.729
86100, 6.737
86200, 6.745
86300, 6.753
86400, 6.761
86500, 6.769
86600, 6.777
86700, 6.785
86800, 6.793
86900, 6.801
87000, 6.809
87100, 6.817
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87900, 6.881
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88100, 6.897
88200, 6.905
88300, 6.913
88400, 6.921
88500, 6.929
88600, 6.937
88700, 6.945
88800, 6.953
88900, 6.961
89000, 6.969
89100, 6.977
89200, 6.985
89300, 6.993
89400, 7.001
89500, 7.009
89600, 7.017
89700, 7.025
89800, 7.033
89900, 7.041
90000, 7.049
90100, 7.057
90200, 7.065
90300, 7.073
90400, 7.081
90500, 7.089
90600, 7.097
90700, 7.105
90800, 7.113
90900, 7.121
91000, 7.129
91100, 7.137
91200, 7.145
9130

TABLE 5
 LEAST SQUARES FIT OF BURN RATE DATA
 ON PROPELLANT 3, CATALYZED

YOUR VALUE FOR REFERENCE PRESSURE IS 21000
 YOUR VALUES OF PRESSURE AND RATE ARE 2100,0.026
 2200,.041
 2500,.072
 2800,.099
 21000,.111
 21500,.148
 20,0

<u>MEASURED DATA</u>		<u>CALCULATED DATA</u>
<u>PRESSURE</u>	<u>RATE</u>	<u>RATE AT 1000</u>
100	.026	.112651
200	.041	.114252
500	.072	.111049
800	.099	.114115
1000	.111	.111
1500	.148	.114323

NO OF POINTS= 6
 SLOPE = .636763
 A = 1.38978E-3
 B500 = 7.27028E-2
 B1000 = .113041
 B1500 = .146341
 STD. DEV. = 1.30216E-3
 PCT OF MEAN= 1.23526

RUNNING TIME: 1.3 SECS 1/3 TIME : 3.0 SECS

TABLE 6
 LEAST SQUARES FIT OF BURN RATE DATA
 ON PROPELLANT 4, CATALYZED

 YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
 YOUR VALUES OF PRESSURE AND RATE ARE ?3
 DELETED

?100,.022
 ?200,.037
 ?300,.048
 ?500,.063
 ?800,.098
 ?1000
 .118

WHAT ?

INCORRECT FORMAT --RETYPE

?1000,.118
 ?1200,.131
 ?1500,.157
 ?0,0

<u>MEASURED DATA</u>		<u>CALCULATED DATA</u>
<u>PRESSURE</u>	<u>RATE</u>	<u>RATE AT 1000</u>
100	.022	.116021
200	.037	.118287
300	.048	.114504
500	.063	.103925
800	.098	.115135
1000	.118	.118
1200	.131	.11484
1500	.157	.11715

NO OF POINTS= 8
 SLOPE = .722114
 A = 7.81674E-4
 B500 = 6.95007E-2
 B1000 = .114648
 B1500 = .153647
 STD. DEV. = 4.59583E-3
 PCT OF MEAN= 4.00864

RUNNING TIME: 2.1 SECS I/O TIME : 3.9 SECS

TABLE 7
 LEAST SQUARES FIT OF BURN RATE DATA
 ON PROPELLANT 5, CONTROL

RONNH

YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
 YOUR VALUES OF PRESSURE AND RATE ARE ?100,.022

?200,.035
 ?300,.045
 ?500,.059
 ?800,.077
 ?1000,.085
 ?1200,.093
 ?1500,.113
 ?0,0

<u>MEASURED DATA</u>		<u>CALCULATED DATA</u>
PRESSURE	RATE	RATE AT 1000
100	.022	8.37733E-2
200	.035	8.91144E-2
300	.045	9.05398E-2
500	.059	8.82379E-2
800	.077	8.76526E-2
1000	.085	.085
1200	.093	8.36573E-2
1500	.113	8.92946E-2

NO OF POINTS= 8
 SLOPE = .580683
 A = 1.57791E-3
 R500 = 5.82545E-2
 R1000 = .087123
 R1500 = .110252
 STD. DEV. = 2.66211E-3
 PCT OF MEAN= 3.05558

RUNNING TIME: 1.9 SECS I/O TIME : 3.6 SECS

TABLE 8
 LEAST SQUARES FIT OF BURN RATE DATA
 ON PROPELLANT 5, CATALYZED

ROSKH

YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
 YOUR VALUES OF PRESSURE AND RATE ARE ?200,.028

?300,.036

?500,.051

?800,.069

?1000,.078

?1200,.087

?1500,.099

?0,0

<u>MEASURED DATA</u>		<u>CALCULATED DATA</u>
<u>PRESSURE</u>	<u>RATE</u>	<u>RATE AT 1000</u>
200	.028	7.74177E-2
300	.036	7.70392E-2
500	.051	7.90301E-2
800	.069	7.94487E-2
1000	.078	.078
1200	.087	7.75326E-2
1500	.099	7.66236E-2

NO OF POINTS= 7
 SLOPE = .631905
 A = 9.89977E-4
 B500 = 5.02478E-2
 B1000 = 7.78644E-2
 B1500 = .100603
 STD. DEV. = 1.03419E-3
 PCT OF MEAN= 1.32819

RUNNING TIME: 1.2 SECS I/O TIME : 3.1 SECS

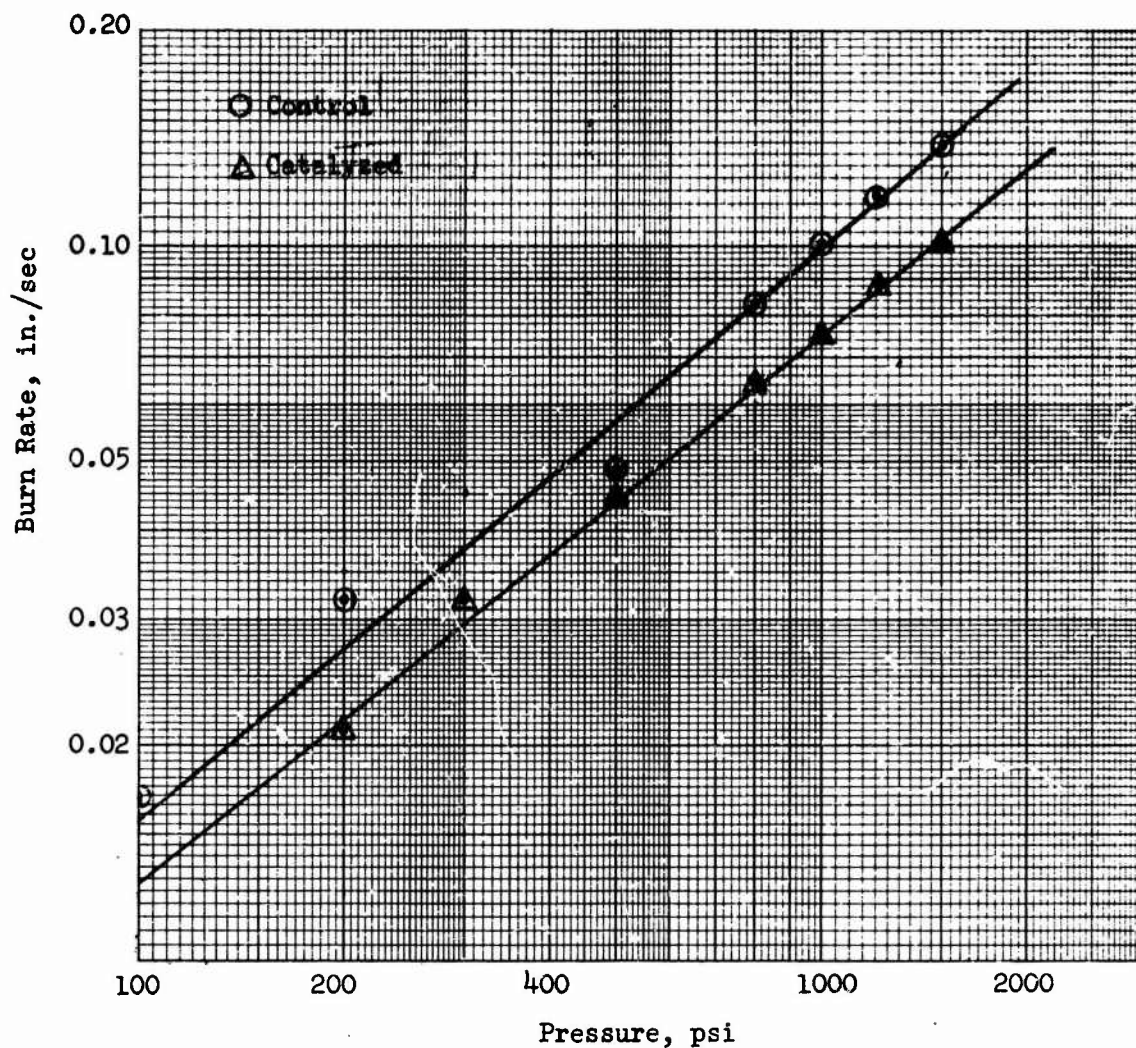


Figure 18. Crawford Bomb Burn Rate Data vs Pressure for Propellants 1A, Control, and 1, Catalyzed*

Figure 18 shows some scatter in data but shows that ammonium chloride reduces the burn rate of an ammonium dichromate catalyzed propellant in the same manner that it reduced the burn rate of an iron catalyzed propellant (milori blue) as shown in the last report.

* Composition presented in first 6-month report. Propellant contains AD and AC catalyst.

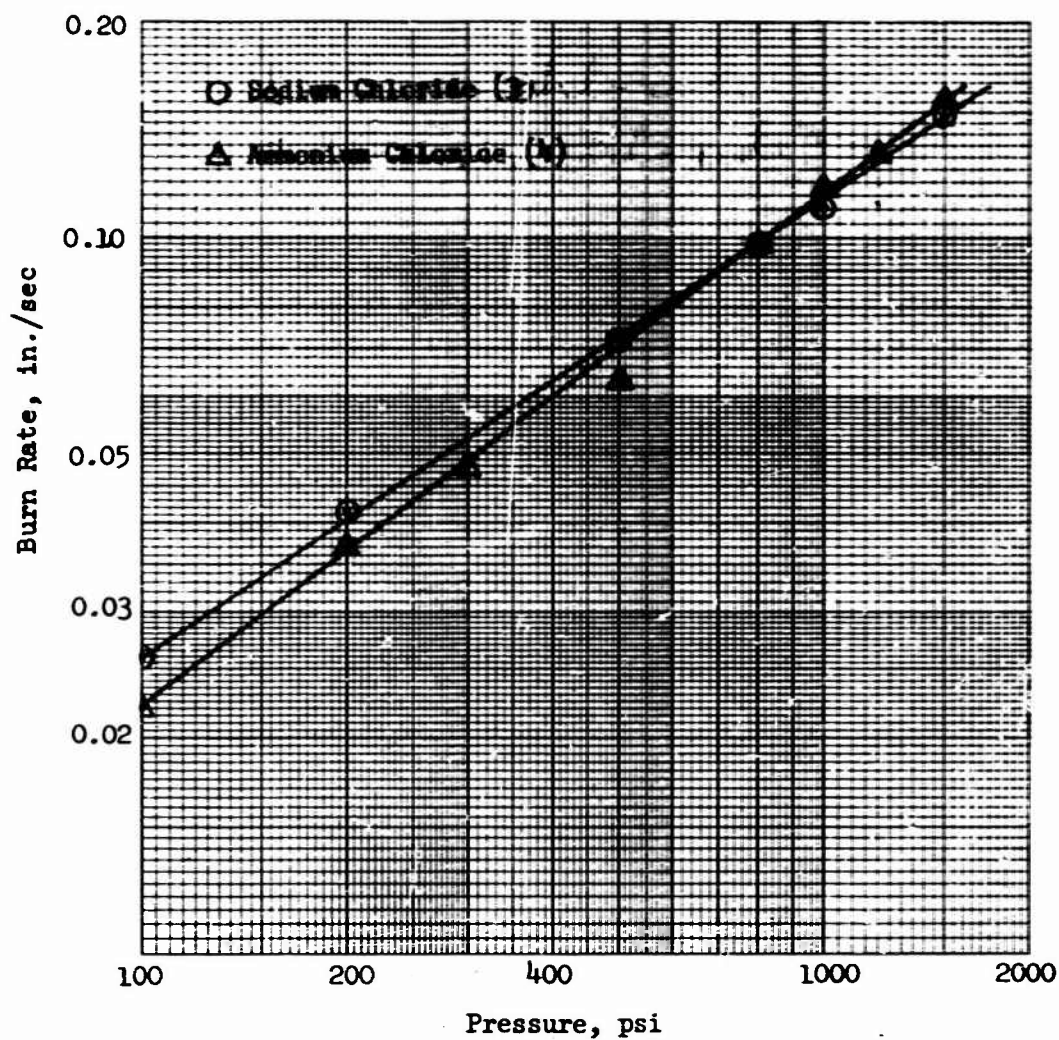


Figure 19. Crawford Bomb Burn Rate Data vs Pressure for Propellants 3 and 4

Figure 19 shows the results obtained from propellants 3 and 4, which contain sodium chloride and ammonium chloride, respectively. The difference between the effects of these two salts is hardly significant. Even though Keenan's results indicated that the cation of the chloride salt was not important, it was considered necessary to demonstrate this in a propellant.

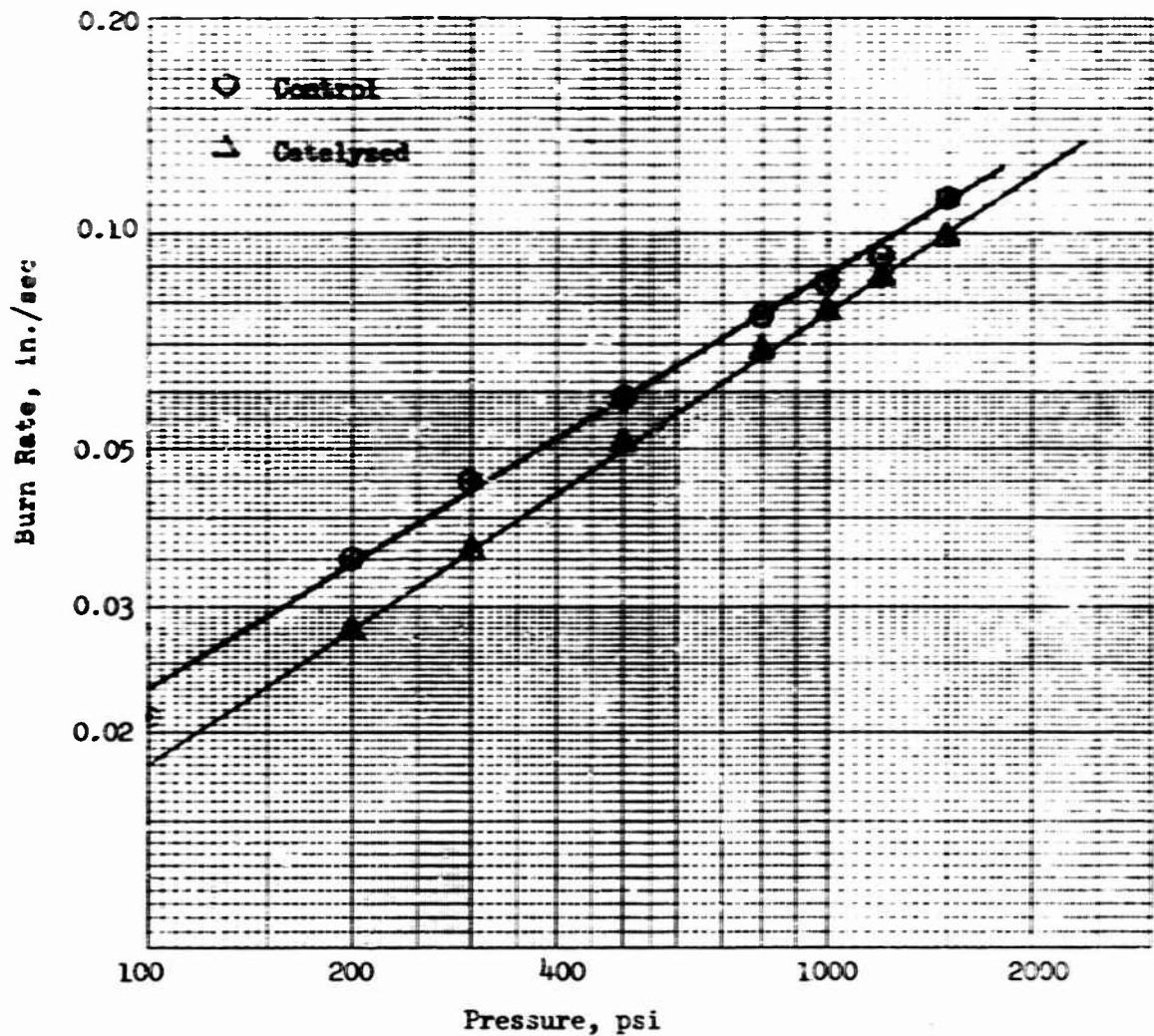


Figure 20. Crawford Bomb Burn Rate Data vs Pressure for Propellants 5, Control, and 5, Catalyzed

Propellant 5 was made to check the effect of the chromium/chloride system in the absence of all other metals (see Fig. 20). All propellants made previously contained magnesium oxide at about a 0.5% level as a part of the propellant cure system. Propellant 5 uses 1,4-bis (trichloromethyl)-benzene as a quaternary curing agent. The difference between propellants 1 and 5 do not appear great. Propellant 5 shows a significantly lower slope of the burn rate vs pressure curve and less depression of burn rate by the chloride at higher pressures.

PROPELLANT MIXES (AMMONIUM PERCHLORATE)

Compositions of castable ammonium perchlorate propellants that have been made are given in Table 9. The oxidizer and catalyst ingredients were thoroughly blended before they were added to the propellant binder. Computer runs are given in Tables 9 through 15, and the resulting data are plotted in Fig. 21 and 22. Propellant 6 containing ammonium chloride showed a depression in burn rate at low pressures; however, the magnitude of the depression is barely significant.

**TABLE 9
COMPOSITION OF AMMONIUM PERCHLORATE PROPELLANTS**

Propellant	Ingredients	Wt %	Actual Weight Used, grams
Control 6	Binder	14.00	63.00
	AP (200 micron)	59.79	269.06
	AP (20 micron)	25.65	115.34
	Ammonium Dichromate	0.58	2.60
			<u>450.00</u>
Catalyzed 6	Binder	14.00	63.00
	AP (200 micron)	57.27	257.72
	AP (20 micron)	25.63	115.34
	Ammonium Dichromate	0.58	2.61
	Ammonium Chloride	2.52	11.34
			<u>450.01</u>
Control 7	Binder	14.00	63.00
	AP (200 micron)	51.25	230.63
	AP (20 micron)	25.63	115.34
	Ammonium Dichromate	0.58	2.61
	Ammonium Nitrate	8.54	38.43
			<u>450.01</u>
Catalyzed 7	Binder	14.00	63.00
	AP (200 micron)	48.73	219.29
	AP (20 micron)	25.63	115.33
	Ammonium Dichromate	0.58	2.61
	Ammonium Nitrate	8.54	38.43
	Ammonium Chloride	2.52	11.34
			<u>450.00</u>

TABLE 10
LEAST SQUARES FIT OF BURN RATE DATA
FROM PROPELLANT 6, CONTROL

READY
RUNNH
YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
YOUR VALUES OF PRESSURE AND RATE ARE ?100,.137
?200,.189
?300,.220
?500,.267
?800,.326
?1000,.357
?1200,.398
?1500,.416
?0,0

<u>MEASURED DATA</u>		<u>CALCULATED DATA</u>
PRESSURE	RATE	RATE AT 1000
100	.137	.353459
200	.189	.366581
300	.22	.361118
500	.267	.355157
800	.326	.357361
1000	.357	.357
1200	.398	.369225
1500	.416	.352055

NO OF POINTS= 8
SLOPE = .411618
A = 2.09015E-2
R500 = .26985
R1000 = .358948
R1500 = .424145
STD. DEV. = 6.17475E-3
PCT OF MEAN= 1.72023

RUNNING TIME: 1.4 SECS I/O TIME : 3.7 SECS

READY
BYE

OFF AT 14:11

TABLE 11
LEAST SQUARES FIT OF BURN RATE DATA
FROM PROPELLANT 6, CATALYZED

READY
RUNNING

YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
YOUR VALUES OF PRESSURE AND RATE ARE ?100,.132

?200,.178
?300,.210
?500,.265
?800,.310
?1000,.343
?1200,.374
?1500,.404
?0,0

PRESSURE	RATE	RATE AT 1000
100	.132	.341144
200	.178	.345661
300	.21	.345013
500	.265	.352679
800	.31	.339879
1000	.343	.343
1200	.374	.346913
1500	.404	.341797

NO OF POINTS= 8
SLOPE = .412364
A = 1.99565E-2
R500 = .258846
R1000 = .34449
R1500 = .407183
STD. DEV. = 4.07968E-3
PCT OF MEAN= 1.18427

RUNNING TIME: 2.4 SECS I/O TIME : 3.2 SECS

READY
BYE

OFF AT 09:01

TABLE 12
 LEAST SQUARES FIT OF BURN RATE DATA
 FROM PROPELLANT 7, CONTROL

RUNNH
 YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
 YOUR VALUES OF PRESSURE AND RATE ARE ?100, .127
 ?200, .166
 ?300, .200
 ?500, .249, -
 ?800, .305
 ?1000, .341
 ?1200, .368
 ?1500, .407
 ?0, 0

PRESSURE	RATE	RATE AT 1000
100	.127	.344832
200	.166	.333675
300	.2	.337176
500	.249	.336347
800	.305	.336
1000	.341	.341
1200	.368	.340016
1500	.407	.341354

NO POINTS= 8
 SLOPE = .433803
 A = 1.69243E-2
 R500 = .250804
 R1000 = .338783
 R1500 = .403934
 STD. DEV. = 3.62497E-3
 PCT OF MEAN= 1.07

RUNNING TIME: 1.7 SECS I/O TIME : 2.5 SECS

READY
 BYE

OFF AT 07:36

TABLE 13
 LEAST SQUARES FIT OF BURN RATE DATA
 FROM PROPELLANT 7, CATALYZED

READY
 RUNNH
 YOUR VALUE FOR REFERENCE PRESSURE IS ?1000
 YOUR VALUES OF PRESSURE AND RATE ARE ?100,.116
 ?200,.154
 ?300,.188
 ?500,.240
 ?800,.300
 ?1000,.338
 ?1200,.369
 ?1500,.403
 ?0.0,0.0

PRESSURE	RATE	RATE AT 1000
100	.116	.34199
200	.154	.327888
300	.188	.330886
500	.24	.332324
800	.3	.333139
1000	.338	.338
1200	.369	.338724
1500	.403	.333135

NO OF POINTS= 8
 SLOPE = .469556
 A = 1.30529E-2
 R500 = .241559
 R1000 = .334483
 R1500 = .40463
 STD. DEV. = 4.65096E-3
 PCT OF MEAN= 1.39049

RUNNING TIME: 2.3 SECS I/O TIME : 3.4 SECS

READY
 BYE

OFF AT 09:01

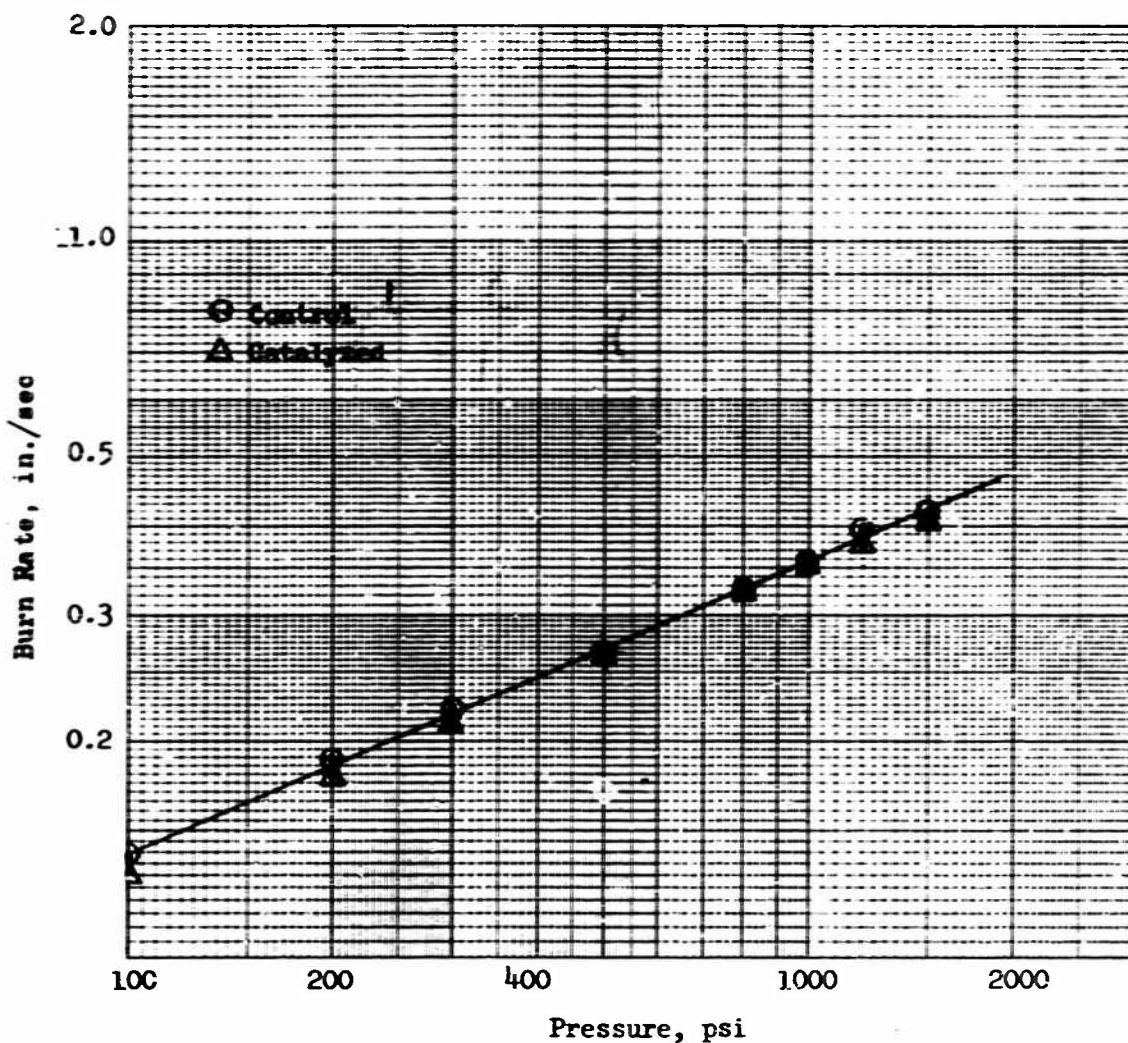


Figure 21. Crawford Bomb Burn Rate Data vs Pressure for Propellants 6, Control, and 6, Catalyzed

Propellant 7 contained the catalyst system and ammonium nitrate. Again, there was a slight depression in burn rate due to the addition of chloride (see Fig. 22). A comparison of controls 6 and 7 indicates the depression due to the ammonium nitrate. It is important to note that 2.5% ammonium chloride is a better burn rate depressant than 8.5% ammonium nitrate.

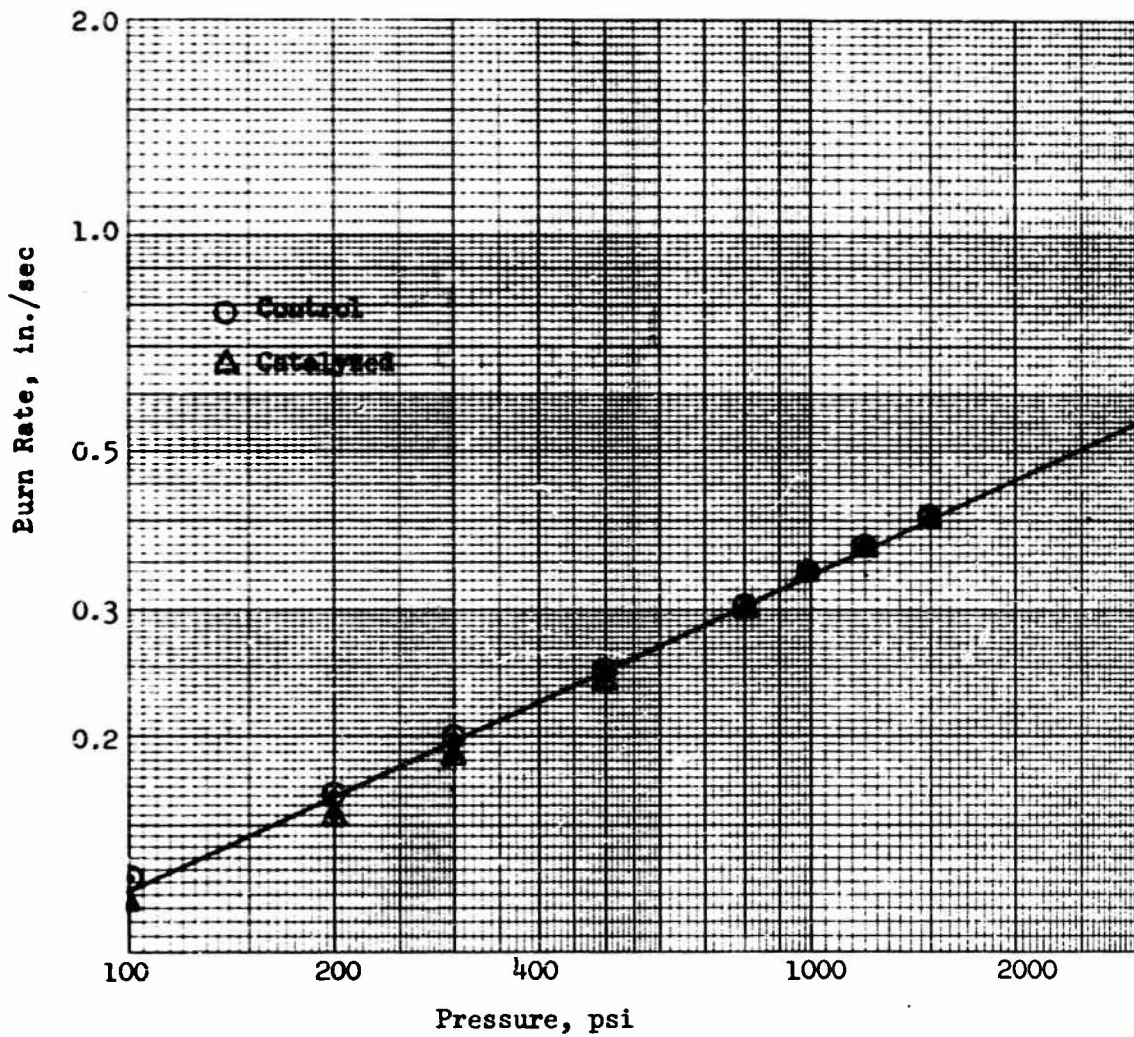


Figure 22. Crawford Bomb Burn Rate Data vs Pressure for Propellants 7, Control, and 7, Catalyzed

DYNAMIC DSC (PROPELLANTS)

Six of the ammonium nitrate propellants made thus far were studied by DSC (Fig. 23 through 28). Dynamic thermograms were run at several heating rates. Agreement between thermograms of these actual propellants and the micromixed pseudo-propellants was exceptionally good.

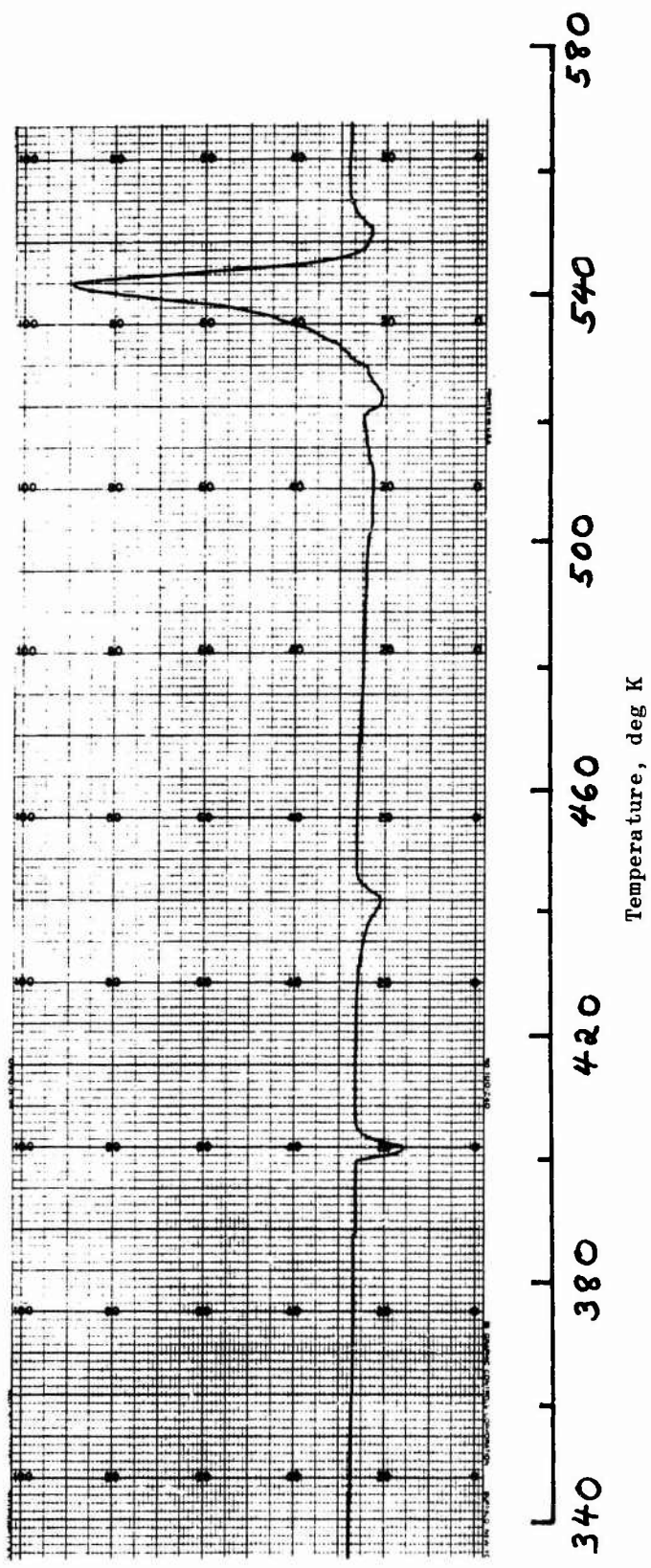


Figure 23. DSC Thermogram of Propellant 1, Control, at 20 deg/min (Sample Weight 3.13 milligrams)

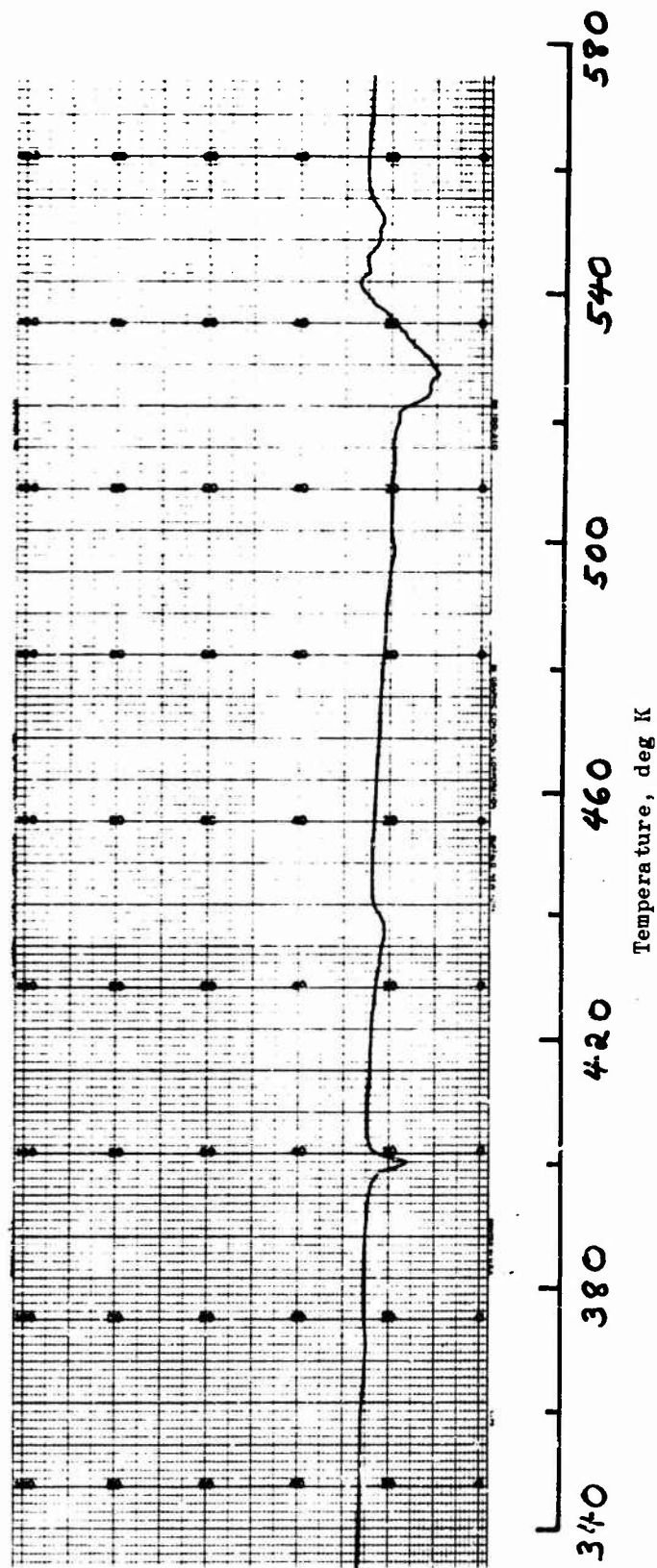


Figure 24. DSC Thermogram of Propellant 1, Catalyzed, at 20 deg/min (Sample Weight 3.22 milligrams)

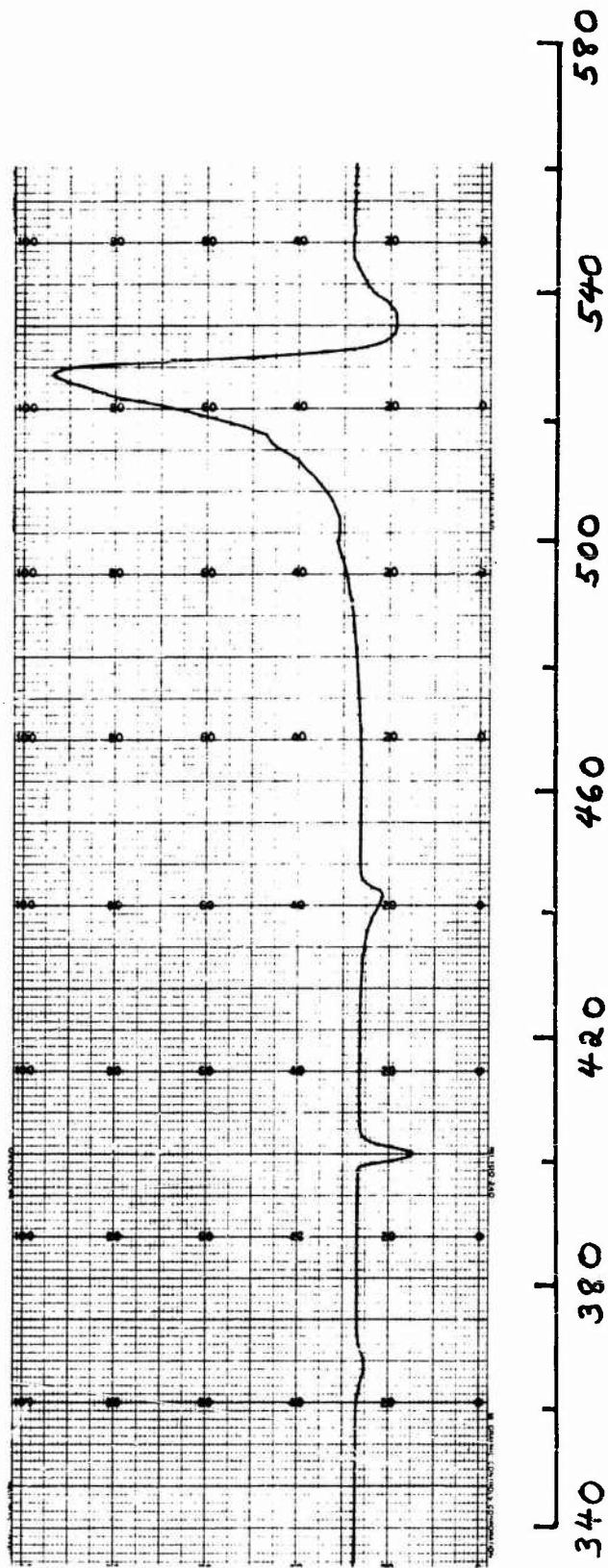


Figure 25. DSC The nogram of Propellant 2, Control, at 20 deg/min (Sample Weight 3.20 milligrams)

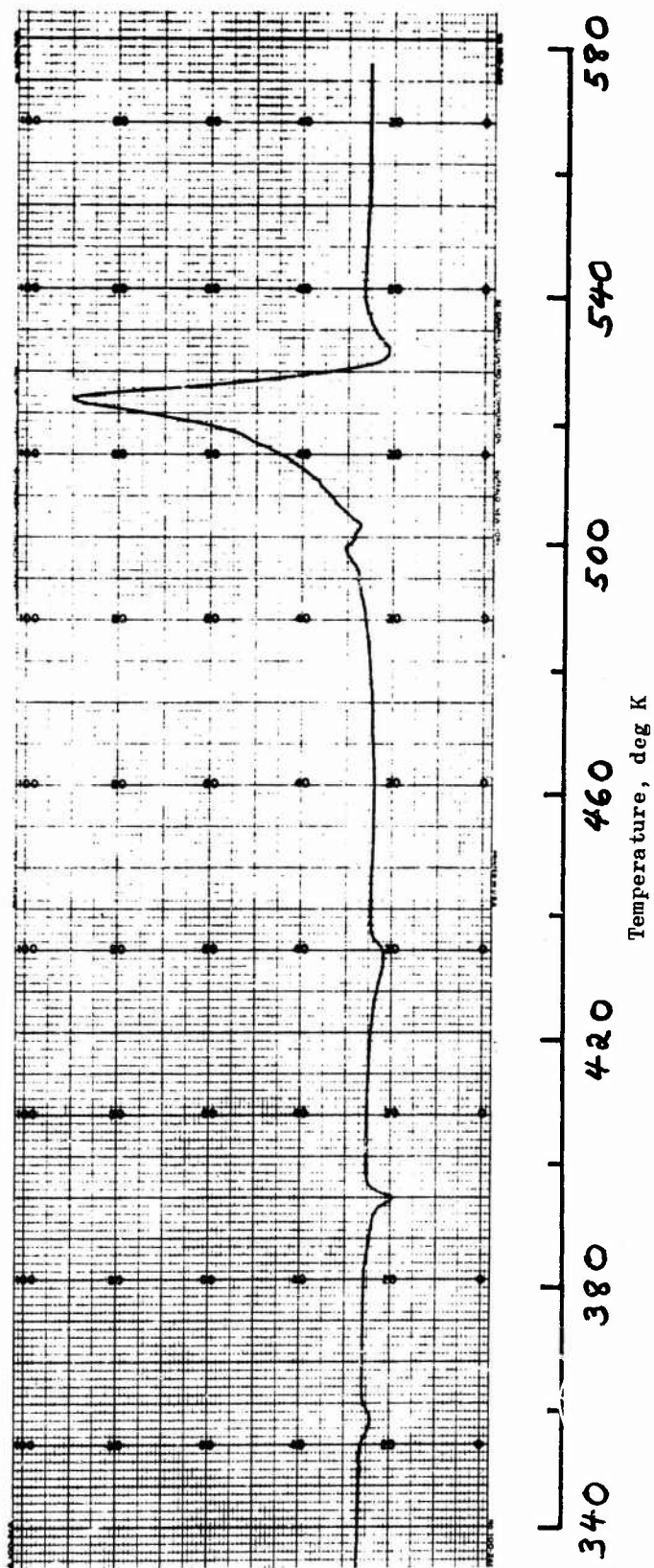
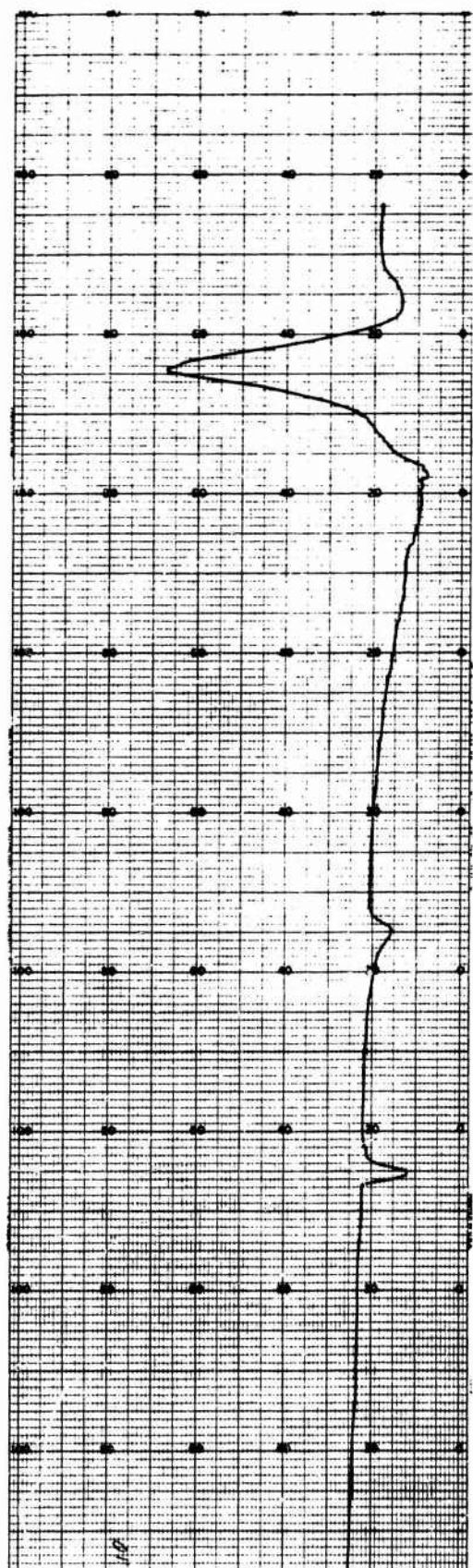


Figure 26. DSC Thermogram of Propellant 2, Catalyzed, at 20 deg/min (Sample Weight 3.28 milligrams)



340 380 420 460 500 540 580
Temperature, deg K

Figure 27. DSC Thermogram of Propellant 1A, Control, at 20 deg/min (Sample Weight 3.07 milligrams)

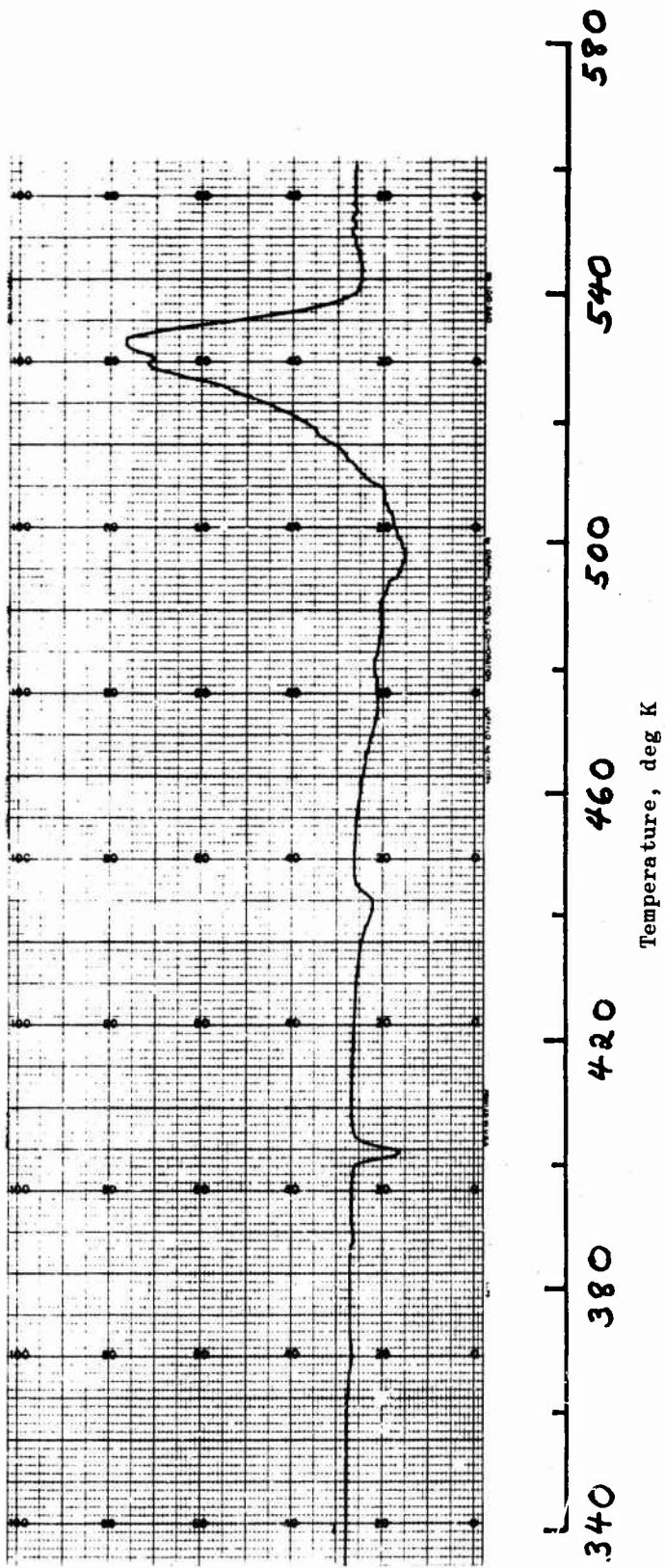


Figure 28. DSC Thermogram of Propellant 4, Catalyzed, at 20 deg/min (Sample Weight 3.39 milligrams)

One of the most significant effects of the catalyst system is shown in Fig. 23 and 24. At a heating rate of 20 deg/min, the exotherm shown in propellant 1, control, is totally suppressed by the addition of the chromium/chloride catalyst system. Figures 25 and 26 show a much smaller reduction with the iron/chloride system.

CO-CRYSTALLIZATION

The melt procedure used by Keenan for the preparation of catalyzed oxidizer is not very practical or safe for the preparation of large quantities (1000 grams) for propellant mixes. Therefore, some time was spent attempting to prepare a co-crystalline ammonium nitrate/ammonium chloride that contained at least 2.5% ammonium chloride.

The general procedure for co-crystallization was as follows:

200 ml of methanol (reagent grade absolute) was brought to boiling in a 500 cc Erlenmeyer flask. 2.75 grams of ammonium chloride (ACS reagent) was dissolved and then 0.18 grams of ammonium dichromate (reagent grade) was dissolved. An additional 200 ml of methanol was added as necessary to maintain solution as 97.1 grams of ammonium nitrate (propellant grade) was added. This solution was allowed to cool to room temperature and then placed in a -15 F freezer overnight. The crystals were then filtered, washed with ether, and dried by suction.

Observation of the crystals showed the chromium to be reduced to chromic oxide and present as separate crystals that could be physically separated by shaking the mixture. An analysis of the upper white crystals showed only a trace of chromium and 0.12% chloride. A number of additional attempts were made to co-crystallize ammonium nitrate and ammonium chloride without the dichromate. In all cases, regardless of the original concentration, the first crop of crystals contained 0.15% or less chloride. A second crop of crystals of higher chloride content could be obtained by adding ether to the mother liquor. The first crop

appeared on microscopic examination to be an isomorphous mixed crystal and the second crop had the appearance of a polymorphous crystal mixture. No more work is planned with ammonium nitrate co-crystallization, but at least one propellant mix is planned with the co-crystallized ammonium nitrate containing 0.15% chloride.

A procedure for co-crystallization of ammonium perchlorate and potassium chloride is already available, and a mixed crystal can be obtained with as much as 10% KCl. Preparation of a sample of AP containing about 2.5% KCl is planned.

CONCLUSIONS

Strand burning rates are continuing to verify the prediction of a burn rate depression by chloride. This prediction was made on the interpretation of DSC data and assuming the importance of condensed phase heat release. Ammonium dichromate is known to be a good burn rate catalyst for ammonium nitrate, but there is no precise knowledge as to how it functions. Gas phase proponents (now dwindling in number) suggest that it functions in the gas phase only. This work does not support that view. The ammonium dichromate catalyzed propellants show a larger exothermic decomposition than propellants without ammonium dichromate, and this exotherm is greatly suppressed by chloride. Suppression of the burn rate of ammonium dichromate catalyzed propellant by chloride represents an indirect support for activity of the catalyst in the condensed phase.

Isothermal TGA showed no induction time with the synergistic decomposition catalyst and a relatively constant rate of decomposition at each temperature studied. It appears that the induction time observed by Keenan was actually a self-heating time. The rate of decomposition at 195 degrees is relatively slow. Keenan used a 195 degree furnace temperature for most of his runs and a relatively large sample (6 grams).

The ammonium nitrate/catalyst mixture has a relatively low thermal conductivity which means that if heat is generated within a sample of any size it is likely to be generated faster than it can be conducted out of the sample, thus leading to the phenomena called self-heating. In this effect the internal temperature of the sample can become run-away. It is likely that the nitrogen sparge which Keenan used to delay the induction time (self-heating) was actually in effect only carrying heat away from the sample convectively so that the sample did not reach a high enough temperature to decompose rapidly.

The DSC and DTA work with micro samples have led us to the conclusion that most of the heat release in the sample is in the gas phase and not the condensed phase. The larger the sample, the more self-heating that would occur because of the vigorous bubbling of the liquid sample from decomposition gases. The micro samples do not have enough contact with the gas phase to absorb its heat.

Propellants made with a quaternary type cure gave essentially the same results as the more normally used cure system containing magnesium oxide.

FUTURE PLANS

During the next 6 months 15 to 20 propellant mixes are planned. These mixes will include a nitrate mix for determination of temperature sensitivity by burning strands at -70, 77 and 170 F, a nitrate mix with co-crystallized AN/AC (0.15% chloride), castable mix with co-crystallized AP/KCl (2.5% KCl), and a nitrate mix with a melt of AN/AC. A number of castable ammonium perchlorate mixes are planned to evaluate the effect of ammonium chloride and potassium chloride on known catalysts such as iron oxide or copper chromite.