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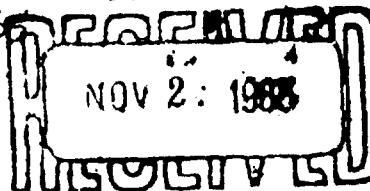
Quarterly Report No. 1

Copy No. 28

"A Study of the Decomposition Mechanism of
Ammonium Perchlorate"

Prepared by: Departments of Chemistry and
Chemical Engineering,
Auburn University

For the period: 1 June - 30 Sept. 1966



Contract No. DA-01-021-AMC-12346(Z), Part I, TISIA E

Birmingham Procurement District, U.S. Army.

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Quarterly Report On:

"A Study of the Decomposition Mechanism of Ammonium
Perchlorate"

Prepared by: Departments of Chemistry and Chemical
Engineering, Auburn University, and
submitted by:

James E. Land,
Project Supervisor

For the Period: 1 June - 30 Sept. 1965

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1. Introduction

This project, which is a continuation of Contract DA-01-009-ORD-1023(Z), Part I, is concerned with the study of the chemical changes that occur during the decomposition of ammonium perchlorate (hereinafter abbreviated AP) produced by the application of heat.

To follow the exo- and endothermic changes which are produced when AP is heated from ambient temperature to approximately 450° C., the technique of differential thermal analysis (DTA) is used.

In particular our interest is centered at present on the effect of various catalytic agents on the mechanism of AP decomposition.

The equipment and experimental procedures, which were described in detail in the Final Report of Contract DA-01-009-ORD-1023(Z), Part I, are still being employed.

2. Current work

During the period of this report our efforts continued with the making of DTA runs at various heating rates on AP samples to which had been added various materials to test the catalytic effect of these additives.

The additives have been selected as to type for the express purpose of trying to prove or disprove the theory of catalytic action for this AP decomposition as proposed in the previously mentioned final report. Since all the catalytic agents, which we plan to investigate, have not been checked, no attempt will be made in this report to correlate the findings.

3. Experimental Materials

The following materials have been used as additives in investigating possible catalytic action. (Note; the letters in parenthesis following the compound name will serve as an abbreviation in the tables which list the results). Composition of these preparations was verified by analysis.

- a. Tetrapyridinezinc perchlorate (ZnPyX). To prepare this compound 5 g. of hydrated zinc perchlorate was added to 10 ml. of dimethoxypropane(DMP) and the mixture stirred for 15 minutes. To this solution was added 10 ml. of pyridine. At first the solution became cloudy but this disappeared on further addition of the pyridine. Five ml. of additional DMP was added and the solution stirred for 30 minutes. On adding 3 ml. of hexane a white precipitate of tetrapyridinezinc perchlorate formed. This was separated by filtration and washed with diethylether.
- b. Copper Chromite (CuCrO_x). The material used here was not a stoichiometric compound. It was rather a mixed oxide mass of uncertain composition.
Preparation was effected by heating together an equal molar mixture of copper(II) chloride and chromium(II) hydroxide until dry.
- c. Copper (I) oxide (Cu_2O). This compound was made by preparing a water solution of 75 g. of potassium sodium tartrate, 75 g. of sodium hydroxide and 50 g. of hydrated copper(II) sulfate. To this solution

was added with stirring 8 g. of hydrazinium hydrosulfate. The copper(I) oxide separated immediately as an insoluble precipitate. It was removed by filtration, washed with water and dried in an oven at 90° C.

- d. Silver Oxide (Ag_2O). a commercial product was used.
- e. Chromium(III) oxide (Cr_2O_3). a commercial product was used.
- f. Sodium acetylacetonate (NaAc). A solution of 20 g. of sodium hydroxide, 50 ml. of water and 200 ml. of methanol was added slowly with stirring to 50 g. of 2,4-pentanedione. The resulting white crystalline precipitate was chilled to 0° C, for about 12 hours, and then filtered. The precipitate was washed with two small portions of cold methanol, filtered and then dried at 90° C.
- g. Iron(II) oxide (FeO). This compound was made by heating iron(II) oxalate, under vacuum, to 300° C. To avoid oxidation it was transferred from one container to another only in a dry box filled with a nitrogen atmosphere. In the DTA runs where this material was mixed with AP an atmosphere of nitrogen was maintained over the sample.
- h. Calcium Oxide (CaO). A commercial product used.
- i. Chromium(II) oxide (CrO). This compound was prepared as follows: An electrolytic cell was made from a 1000 ml. beaker filled with enough mercury to cover the bottom. The mercury, which was the cathode in this cell, gave a surface area of 41 square centimeters.

Platinum of about 50 square centimeter area was used for the anodes. A mechanical stirrer was used to aggitate the solution.

The electrolytic solution was composed fo 250 g. of CrO_3 and 2.5 g of 95% sulfuric acid in enough water to give a total volume of one liter. A voltage drop of 6.5 volts was used and 8.5 amps. of current passed through the cell for 14 hours.

At the end of the electrolysis the mercury cathode was removed, dissolved in nitric acid, thereby leaving behind the CrO as an insoluble black powder. This powder was filtered, washed and stored under a nitrogen atmosphere.

- j. Tetramminezinc perchlorate (ZnAmX). To prepare this compound an excess of 6 normal ammonia solution was added to a solution of 4 g. of hydrated zinc perchlorate. The white complex precipitated immediately. It was separated by filtration and air dried.
- k. Magnesium oxide (MgO). A commercial product was used.
- l. Tetramine copper(II) perchlorate (CuAmX). This material was made by adding a solution of perchloric acid to copper(II) carbonate until only a small residue of the solid carbonate remained undissolved. This excess solid was removed by filtration. To the filtered solution conc. ammonium hydroxide was added with stirring. Very soon a blue crystalline mass separated from solution. The crystals were removed by filtration. washed with ammonia water and

dried over calcium oxide.

- m. Hexamminecadmium perchlorate (CdAmX). To make this compound it was first necessary to make hydrated cadmium perchlorate. This was accomplished by starting with a cadmium nitrate solution from which cadmium hydroxide was precipitated with potassium hydroxide. The cadmium hydroxide after separation and washing was dissolved in perchloric acid solution. This resulting solution after evaporation to one-third original volume deposited white crystalline hexaquocadmium perchlorate.

5 g. of the hydrated cadmium perchlorate was added to 10 ml of DMP and stirred for 2 hours. Anhydrous ammonia gas was bubbled through the resulting solution for 2 hours. The white hexammine complex separated immediately.

- n. Hexamminecobalt(III) perchlorate (CoAmX). To obtain this compound we first made by standard procedures the hexamminecobalt(III) chloride. Reaction of this chloride with silver perchlorate in solution produced a precipitate of silver chloride thereby leaving the desired material in solution. On evaporation and cooling the crystals were obtained. Analysis indicated no chloride ions present in the product.
- o. Tricobalt tetroxide (Co_3O_4). This material was produced by heating cobalt(II) carbonate at a temperature of 500°C for a period of two days.

- p. Hexamminenickel(II) perchlorate (NiAmX). A method for making this compound was based upon one given in the literature for making the corresponding bromide compound.

To 50 g. of NiCl_2 was added an excess of NaOH solution and the resulting precipitate filtered and washed several times with water. To this precipitate of Ni(OH)_2 was added perchloric acid solution such that a small amount of precipitate was left to insure that all of the acid had been neutralized. This excess precipitate was removed by filtration. The solution of nickel(II) perchlorate was cooled to 0°C . and ammonia gas bubbled through it slowly for six hours. A blue-violet crystalline mass settled out. The crystals were removed by filtration, washed with ammonia water, and dried over calcium oxide.

- q. Tris(ethylenediamine) zinc perchlorate. (ZnEnP).

Five grams of zinc perchlorate, hydrated was added to 20 ml. of DMP and the mixture stirred for 30 minutes. Next 6 ml. of ethylenediamine were added slowly. A curdy white precipitate formed. This was removed by filtration, washed with small portions of diethyl ether and air dried.

- r. Nickel(II) oxide. (NiO-A) represents a commercial product that was used as taken from the bottle. (NiO-B) represents the same material but heated at 550°C for 12 hours before use.

4. Tabulated Results

In Table I are presented the results of DTA runs made with the selected additives and AP.

The data in this table is listed as follows:

Column (1) gives the additive under investigation for its possible catalytic effect. Five per cent by weight was added to the AP sample. All runs were made at atmospheric pressure and open to the air except in those cases where an asterisk (*) appears with the additive abbreviation.

Column (2) lists the size of the AP particles (cf. page 25 of the final report for Project 1023(z), Part I).

Column (3) gives our sample number to facilitate locating the DTA plot when needed for reference. Column (4) shows the heating rate in $^{\circ}\text{C.}$ per minute. This was the setting on the temperature programmer and was not the measured slope of the heating curve trace. Columns marked T_1 , T_2 , T_3 , etc. are the peak temperatures in $^{\circ}\text{C.}$ as read from left to right on the DTA plot. Only T_1 , which is the crystal transformation, is endothermic.

Table II gives the results of DTA runs made on certain of the pure additives used in the catalytic studies. This information is necessary since some of these compounds are capable of undergoing decomposition and such peaks would then be superimposed on the DTA plot of the AP decomposition. Those additive studies and not listed in Table II show no change over the temperature range studied.

The only change in column headings in Table II as compared to Table I is that Column (2) gives the weight in grams of the sample heated. Where no sign is recorded before the temperature value a positive sign is understood and this means that it is a peak temperature of an exotherm. A negative sign implies an endotherm.

Table I

Peak temperatures from DTA runs of AP charges containing additives.

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
(ZnPyX)	F	4-51-3	2	237.1	291.0		
"	F	4-52-1	4	241.1	311.8		
"	F	4-52-2	10	240.3	352.5		
(ZnPyX)	M	4-52-3	2	239.5	289.9		
"	M	4-53-3	4	240.3	310.6		
"	M	4-54-1	10	244.2	333.9		
(ZnPyX)	C	4-53-1	2	237.9	289.1		
"	C	4-53-3	4	241.1	311.4		
"	C	4-54-2	10	242.6	333.2		
(CuCrOx)	F	4-56-1	2	238.3	353.7		
"	F	4-56-2	4	241.1	349.9		
"	F	4-57-2	10	243.4	347.2		
(CuCrOx)	M	4-57-4	2	241.1	365.0		
"	M	4-56-3	4	241.4	351.8		
"	M	4-57-3	10	243.0	363.9		
(CuCrOx)	C	4-58-1	2	237.9	352.2		
"	C	4-58-2	4	240.7	355.6		
"	C	4-57-4	10	244.6	365.0		
(Cu ₂ O)	F	4-60-1	2	237.5	314.7		
"	F	4-63-3	4	241.1	337.0		
"	F	4-63-1	10	240.3	337.0		
(Cu ₂ O)	M	4-60-2	2	237.1	322.9		
"	M	4-63-2	4	241.1	328.2		
"	M	4-66-1	10	241.1	337.7		
(Cu ₂ O)	C	4-66-4	2	237.9	356.8		
"	C	4-66-2	4	241.1	324.8		
"	C	4-66-3	10	244.2	333.2		
(Ag ₂ O)	F	4-69-1	2	237.5	330.5		
"	F	4-67-4	4	238.3	352.2		
"	F	4-69-3	10	241.1	369.5		
(Ag ₂ O)	M	4-70-1	2	237.9	318.7		
"	M	4-69-2	4	239.9	349.5		
"	M	4-71-4	10	238.7	364.3		

Table I Continued

Peak temperatures from DTA runs of AP charges containing additives.

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
(Ag ₂ O)	C	4-71-1	2	237.9	325.6		
"	C	4-71-2	4	240.7	358.2		
"	C	4-71-3	10	241.4	374.4		
(Cr ₂ O ₃)	F	4-75-2	2	239.1	295.3	333.2	
"	F	4-72-4	4	240.3	318.3		
"	F	4-74-1	10	243.8	344.2		
(Cr ₂ O ₃)	M	4-73-2	2	240.3	291.4	348.0	
"	M	4-74-2	4	242.2	307.2	357.1	
"	M	4-75-3	10	243.8	375.9		
(Cr ₂ O ₃)	C	4-74-3	2	240.7	287.1		
"	C	4-75-1	4	241.4	305.3	352.9	
"	C	4-75-4	10	243.8	371.0	420.6	
(NaAc)	F	4-78-2	2	238.7	328.6	406.7	
"	F	4-77-2	4	239.9	341.9	412.0	
"	F	4-76-4	10	239.9	352.9	410.9	
(NaAc)	M	4-78-1	2	238.3	396.6		
"	M	4-77-3	4	238.3	341.5	408.6	
"	M	4-79-1	10	238.3	354.8	432.9	
(NaAc)	C	4-79-3	2	240.3	407.1		
"	C	4-79-2	4	239.5	412.4		
"	C	4-79-4	10	238.3	348.4	428.0	
(FeO)	F	4-83-3	2	237.9	273.1	343.4	
"	F	4-83-2	4	241.1	314.9	349.1	
"	F	4-83-1	10	239.5	321.8	365.0	
(FeO)	M	4-82-2	2	237.1	263.4	288.7	324.4
"	M	4-81-4	4	241.1	304.9	368.4	
"	M	4-81-5	10	237.1	327.8	371.0	
(FeO)	C	4-80-3	2	238.7	347.6		
"	C	4-80-2	4	241.1	298.7	358.6	
"	C	4-80-1	10	238.3	322.5	380.1	
(CaO)	F	4-84-1	2	237.5	346.5		
"	F	4-81-1	4	237.1	359.0	447.9	
"	F	4-86-2	10	241.3	365.5	460.9	

Table I Continued

Peak temperatures from DTA runs of LP changes containing additives.

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
(CaO)	M	4-84-2	2	237.1	349.5		
"	M	4-85-2	4	240.3	360.5	450.5	
"	M	4-85-3	10	241.1	382.8	464.9	
(CaO)	C	4-85-1	2	237.1	345.3		
"	C	4-86-3	4	241.1	361.6	451.6	
"	C	4-86-1	10	241.1	386.1	465.7	
(CrO)	F	4-87-2	2	240.3	255.6	279.7	318.0
"	F	4-88-1	4	241.1	264.5	291.0	326.3
"	F	4-87-3	10	243.0	304.1	335.4	412.4
(CrO)	M	4-88-2	2	238.3	277.4	316.4	399.3
"	M	4-90-1	4	241.1	292.2	230.9	428.9
"	M	4-88-33	10	241.8	306.4	343.4	436.3
(CrO)	C	4-90-3	2	240.3	280.9	341.9	424.4
"	C	4-91-1	4	241.4	292.2	334.7	439.3
"	C	4-90-2	10	243.8	306.8	348.4	447.1
(ZnAmX)	F	3-89-1	2	247.0	353.7		
"	F	3-88-1	4	251.7	366.1		
"	F	3-96-2	10	249.0	380.9		
(ZnAmX)	M	3-93-1	2	246.2	306.4		
"	M	3-82-3	4	248.2	366.9		
"	M	3-99-1	10	287.9	410.1		
(ZnAmX)	C	3-96-1	2	247.8	311.0		
"	C	3-97-1	4	245.0	329.4		
"	C	3-98-1	10	284.8	405.6		
(ZnAmX)*	F	3-90-1	2	249.4	357.9		
"	F	3-91-1	4	248.6	367.6		
"	F	3-92-1	10	248.6	383.1		
(ZnAmX)*	M	3-94-2	2	247.8	326.0		
"	M	3-95-1	4	249.4	353.7		
"	M	3-95-2	10	247.0	372.5		

*Was run under N₂ pressure 60mm^{Hg} in excess of atmospheric pressure

Table I Continued

Peak temperatures from DTA runs of AP charges containing additives.

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
(ZnAmX)*	C	3-98-2	2	240.0	291.8		
"	C	3-97-2	4	236.0	324.4		
"	C	3-99-2	10	240.0	347.1		
(MgO)	F	4-29-1	2	240.7	271.6	353.3	
"	F	4-26-1	4	243.0	378.1		
"	F	4-29-2	10	241.8	390.6		
(MgO)	M	4-1-2	2	237.9	284.4	308.3	326.3
"	M	4-2-2	4	240.3	292.2	327.1	366.5
"	M	4-2-1	10	249.0	387.6		
(MgO)	C	4-29-3	2	241.8	314.9	341.5	
"	C	4-28-1	4	239.5	335.8	349.5	
"	C	4-28-2	10	239.9	322.5	373.6	
(CuAmX)	F	4-7-1	2	240.3	382.2		
"	F	4-7-2	4	242.2	307.6	348.7	
"	F	4-7-3	10	245.0	280.9	345.3	
(CuAmX)	M	4-8-1	2	239.9	270.4	354.1	373.6
"	M	4-8-2	4	240.7	280.9	350.6	
"	M	4-8-3	10	243.8	EXPLOSION		
(CuAmX)	C	4-9-1	2	239.1	303.7	361.3	
"	C	4-9-2	4	239.5	285.2	352.2	
"	C	--	10	(not run)			
(CdAmX)	F	4-10-3	2	237.9	331.3	371.8	
"	F	4-11-1	4	240.2	350.1	398.1	
"	F	4-11-2	10	245.0	363.1	428.5	

*Was run under N₂ pressure 60mm in excess of atmospheric pressure

Table I Continued

Peak temperatures from DTA runs of AP changes containing additives.

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
(CdAmX)	M	4-12-1	2	239.5	322.5	371.0	
"	M	4-12-3	4	241.8	348.4	411.6	
"	M	4-12-2	10	243.4	363.1	428.9	
(CdAmX)	C	4-15-4	2	241.1	319.9	382.0	
"	C	4-14-2	4	242.2	341.1	419.9	
"	C	4-14-3	10	243.0	356.7	428.1	
(CoAmX)	F	4-17-2	2	239.1	327.1		
"	F	4-17-3	4	244.2	352.5		
"	F	4-17-1	10	245.0	366.9		
(CoAmX)	M	4-18-2	2	240.7	336.2		
"	M	4-18-1	4	241.1	346.5		
"	M	4-18-3	10	243.4	373.6		
(CoAmX)	C	4-19-4	2	241.4	338.1		
"	C	4-19-5	4	242.2	357.9		
"	C	4-20-1	10	244.6	367.6		
(Co ₃ O ₄)	F	4-21-1	2	242.6	329.8		
"	F	4-21-2	4	240.7	300.6	360.5	401.1
"	F	4-21-3	10	241.4	305.3		
(Co ₃ O ₄)	M	4-22-1	2	238.7	296.8		
"	M	4-22-2	4	241.8	309.9		
"	M	4-22-3	10	242.2	303.3		
(Co ₃ O ₄)	C	4-23-1	2	239.5	311.0		
"	C	4-24-1	4	241.1	324.1	341.1	412.4
"	C	4-25-1	10	242.9	327.9		
(NiAmX)	F	4-31-3	2	240.6	311.0	372.9	
"	F	4-31-4	4	241.8	268.5	333.9	421.8
"	F	4-32-1	10	243.8	277.8	350.3	438.9
(NiAmX)	M	4-32-2	2	237.9	248.2	314.1	383.1
"	M	4-32-3	4	244.6	263.4	322.5	416.9
"	M	4-35-2	10	243.8	329.7	453.5	
(NiAmX)	C	4-34-2	2	234.3	397.0		
"	C	4-34-1	4	237.5	307.6	428.1	
"	C	4-34-3	10	239.9	327.1	442.6	

Table I Continued

Peak Temperatures from DTA runs of AP charges containing additives.

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
(ZnEnP)	F	4-38-1	2	239.5	334.7		
"	F	4-37-1	4	237.9	347.6		
"	F	4-38-2	10	239.9	363.5		
(ZnEnP)	M	4-37-2	2	239.1	350.6		
"	M	4-37-3	4	240.3	356.9		
"	M	4-37-4	10	241.8	378.9		
(ZnEnP)	C	4-39-2	2	241.4	348.0		
"	C	4-39-3	4	241.4	360.5		
"	C	4-40-1	10	241.1	378.9		
(NiO-A)	F	4-41-1	2	238.3	354.8		
"	F	4-44-2	4	241.8	346.1	406.8	
"	F	4-49-1	10	244.2	363.9	427.8	
(NiO-A)	M	4-44-1	2	240.3	390.6		
"	M	4-42-1	4	239.5	412.0	425.1	
"	M	4-49-2	10	242.6	437.0		
(NiO-A)	C	4-45-1	2	237.9	323.7	389.9	
"	C	4-44-3	4	239.1	416.1		
"	C	4-49-3	10	241.1	419.1		
(NiO-B)	F	4-47-1	2	240.4	332.8	383.1	
"	F	4-48-2	4	241.1	349.5	405.3	
"	F	4-50-1	10	242.2	364.6	418.0	
(NiO-B)	M	4-47-2	2	239.9	327.1	378.1	
"	M	4-43-1	4	241.4	393.3		
"	M	4-50-2	10	242.6	357.5	421.0	
(NiO-B)	C	4-48-1	2	238.7	382.8	400.0	
"	C	4-48-3	4	237.9	408.6		
"	C	4-50-3	10	245.0	445.6		
(ZnO)	M	3-89-1	4	249.0	338.8		
(MgO)*	F	3-100-3	2	238.5	337.7	353.5	
"	F	3-100-2	10	243.3	394.4		

Table II

Peak Temperatures, exo- and endotherms, as taken from DTA runs on certain pure additive, catalytic compounds tested with AP.

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
(NiAmX)	0.005	4-30-4	4	269.2			
"	0.020	4-31-1	4	272.3	219.1		
"	0.050	4-31.2	4	109.4	275.5		
(ZnEnP)	0.005	4-35-1	4	283.6			
"	0.020	4-36-1	4	279.0			
"	0.050	4-35.3	4	279.4			
(ZnPyX)	0.005	4-50-4	4	-	-		
"	0.020	4-51-1	4	386.5			
"	0.050	4-51-2	4	228.7	384.6		
(CoAmX)	0.050	4-25-2	4	(-)112.0	273.5	293.0	303.3
(note: this compound also gave T ₅ =314.1 and T ₆ =484.2							
(CdAmX)	0.050	4-25-3	4	(-)164.0	-302.6	407.5	442.3
(note: this compound also gave T ₅ =(-)501.2							
(CdO)	0.050	4-26-3	4	(-)91.0	396.3		
(CuAmX)	0.005	4-4-1	4	274.7	288.7	324.1	
"	0.020	4-5-1	4	276.2	294.5	326.3	
"	0.050	4-6-1	4	EXPLOSION			
(CoAmX)	0.050	4-16-3	4	278.6	303.0	473.5	

Note: The following gave no exo- or endotherms: CuO; Co₃O₄; MgO; (NiO-); Cu₂O.