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STUDIES INTO THE THERMAL STABILITY AND REACTIVITY OF AMMONIUM NITRATE PART 3. CHARACTERIZATION OF AMMONIUM NITRATE AND METAL REACTION PRODUCTS

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STUDIES INTO THE THERMAL STABILITY AND REACTIVITY OF AMMONIUM NITRATE
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by

P.P. Lee*, R.M. Snippe** and R.R. Vandebeek***

ABSTRACT

This report deals with research into the reactivity of ammonium nitrate-metal systems at temperatures below the melting point of ammonium nitrate.

The lowest reaction temperature has been established for each of the metallic elements in reaction with ammonium nitrate.

Various methods of analysis, both qualitative and quantitative, have been employed to identify the reaction products.

Key words: ammonium nitrate, Cu, Zn, Ni, Cr, Pb, Al, Fe, thermal

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ÉTUDES PORTANT SUR LA STABILITÉ THERMIQUE ET LA RÉACTIVITÉ DU NITRATE D'AMMONIUM PARTIE 3. CARACTÉRISATION DES PRODUITS OBTENUS LORS DE LA RÉACTION DU NITRATE D'AMMONIUM AVEC DIVERS MÉTAUX

par

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RÉSUMÉ

Cette étude traite de la réactivité des systèmes nitrate d'ammonium-métaux à des températures au-dessous du point de fusion du nitrate d'ammonium.

Nous avons établi le niveau inférieur de température auquel réagit chaque élément métallique avec le nitrate d'ammonium.

Diverses méthodes qualitatives et quantitatives furent utilisées pour identifier les produits de réaction.

Mots-clés: nitrate d'ammonium, Cu, Zn, Ni, Cr, Pb, Al, Fe, thermique

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INTRODUCTION

The stability of ammonium nitrate (AN) has been studied for decades. Investigation of accidents such as fires or explosions occuring during storage have not establish definite causes in their occurences. The effect of metals on the stability of AN had not been studied previously in detail. As a consequence of this, the Canadian Explosives Research Laboratory is investigating the reactivity of AN and metal additives more extensively. Two parts of the studies have been reported [1,2].

In this study, experiments were performed on AN with various metal additives under controlled conditions. The methods of analysis are as in the literature [3-16] and the analytical results of AN-metal reaction products are reported.

EXPERIMENTAL

REACTION TEMPERATURE

The reaction of ammonium nitrate-metal systems at a temperature range below the melting point of AN has been studied previously and the lowest temperature at which the reaction took place was established using accelerating rate calorimetry [1]. The elements covered in this report and their working temperature ranges with AN are given in the table below:

TABLE 1 - MINIMUM TEMPERATURES FOR AN-METAL REACTIONS

Metal Element	Minimum Temperature Range/°C
Cu	160 - 165
Zn	135 - 140
Ni	135 - 140
Cr	160 - 165
Pb	115 - 120
Al	165 - 170
Fe	165 - 170

REACTION PRODUCTS

Previous experiments have shown that some metals react with ammonium nitrate at a temperature below the melting point of AN. The products of the AN-metal system need to be characterized in order to extract more information on their properties and to understand how the reaction occurred.

The AN-metal systems were subjected to pre-determined temperatures for a length of 16 hours under open and confined environments. A list of known possible products (based on elemental composition) was matched against the physical characteristics of the products. The products were analyzed by qualitative and quantitative methods.

QUALITATIVE ANALYSIS

(1) Solubility

The appearance of every reaction mixture was recorded according to texture and colour. The water solubility of each mixture and the appearance of the resulting solution and insoluble residue were noted. The water insoluble residue was treated with an acid solution to determine any acid solubility. Again, the solution's colour and the acid insoluble residue's appearance were noted. Finally, if any other peculiar characteristics (e.g. odour) were observed, they were recorded.

(2) pH

It was only important to record pH in situations where a precipitate would form in the water solutions. In these situations, the initial pH of the solution with precipitate was recorded; the pH was adjusted so as to just dissolve the precipitate; and the final pH was recorded. The precipitate was, in most cases, due to the metal hydroxide

which meant that the dissolving medium was an acid solution. In order to avoid introducing competing ions to the solution, the acid of choice was nitric acid (HNO_3) since it shares the nitrate (NO_3) ion with AN.

(3) Melting Point

The melting points of each reaction product were determined on a Gallenkamp melting point apparatus. The appearance of the final product would dictate how that product would be treated. If the product was homogeneous throughout, a single melting point was taken. If two distinct products were evident, two separate melting points were taken. If a reaction had not occured, the melting points of the AN alone and of the AN plus metal were taken. Also, when deemed necessary, the melting points of the insoluble residues were taken.

(4) Infrared Spectroscopy

The infrared (IR) spectrum of each product and residue was recorded, providing the state of the product was such that a spectrum could be taken, on a Perkin-Elmer 735B Infrared Spectrophotometer. Each sample was run as a pressed disk in a KBr matrix at a concentration of 1-2%.

(5) Ultraviolet Spectrophotometry

After the samples had been put into water and filtered, the solutions were analyzed by ultraviolet (UV) spectroscopy on a Bausch and Lomb Spectronic 200UV. Each sample was run against a reference of distilled water. The spectra showed the presence of nitrate in the range of 300-305nm and also of some metal salts in the area of 340-390nm. It should be noted that if the concentration of nitrate was too great its wavelength would shift from 300 to 260nm. Thus, if an absorbance was detected at 260nm but not at 300nm, it was attributed to the nitrate ion.

QUANTITATIVE ANALYSIS

All weighings were done on a Sartorius analytical balance. Volumes were measured in graduated cylinders, pipettes, burettes and volumetric flasks.

(1) Weight Determination

Prior to and immediately following filtration of both the water and acid insoluble residues, various weight determinations were made. Initially, the weight percentage of metal in the AN-metal system was calculated. After the reaction, the percent weight loss for the entire system was found. Finally, the weights of the insoluble residues were taken.

(2) Kjeldahl Determination of Ammonia

Ammonium nitrate is very water soluble as is any metal salt derived from an AN-metal reaction. Thus, an ammonia test can be performed on the water solution to establish the percent recovery of ammonia (assuming 100% AN as starting reagent). The procedure, described in Appendix 1, is based upon the reaction:

$$NH_4^+ + OH^- \rightarrow NH_3(g) + H_2O$$

(3) UV Determination of Nitrate

A quantitative UV analysis of nitrate in the water solution is only possible if there are no interfering absorbances and if the maximum nitrate absorbance is at the same wavelength as the standard. The standard is composed of reagent grade AN dissolved in water and diluted to a known volume. As before, distilled water was used as the reference solution.

(4) Nitron Precipitation of Nitrate

Nitron (1,4-diphenyl-3,5-endoanilodihydrotriazol; $C_{20}H_{16}N_4$) can

be used as a gravimetric agent in the determination of nitrate. As it has a rather high molecular weight (312.2) compared to the resulting nitrate precipitate (375.2), any minor errors in weighing are not evident in the final nitrate calculation. The procedure and calculations for finding the percentage nitrate recovery are given in Appendix 2.

(5) Lead Sulphate Precipitation of Lead

Lead cations can be quantitatively precipitated out of solution as lead sulphate. An alternate determination to atomic absorption was established for lead in order to verify the results of both determinations. Both methods gave reproducable values and justified the adoption of lead sulphate precipitation as a means of analysis. The procedure and calculations for this gravimetric analysis are given in Appendix 3.

(6) Atomic Absorption Determination of Metals (AA)

The percentage of metal in solution was analyzed on a Perkin-Elmer Absorption Spectrophotometer 603. The amounts in both the water and acid solutions were determined when run against a set of standards for the particular metal. The concentration of the standards was set at 5.0, 25.0 and 50.0 parts per million (ppm). Readings were taken in both concentration and absorption units as the concentration readings tended to drift over a range of 4-5 ppm. When read in absorption units, the concentrations of the solutions were determined through linear regression. Both absorption and concentration units gave similar results, yet,due to its consistency, the absorption readings were favoured.

RESULTS

The AN-metal systems were subjected to the pre-determined temperatures for a length of 16 hours. The products of these reactions were analyzed qualitatively and quantitatively. A list of known possible

products (based on elemental composition) was matched against the physical characteristics of the products. The closest match was given initial identification. Each element analyzed is discussed here.

COPPER

Copper was reacted with AN at metal weight percentages of 10 and 40 in both open and closed environments. It was analyzed qualitatively with respect to its appearance, pH, melting point, IR and UV spectra. Table 2 gives a summary of the experimental results and possible corresponding products cited in the literature are given in Table 3.

Quantitative analysis (through weight, Kjeldahl and AA) was also conducted. The calculation of the molar ratio of AN to metal after reaction was based on the results of NH_3 found by Kjeldahl method and the metal contents by atomic absorption. The molar ratios of AN to metal, both before and after the reaction, are given in Table 4.

TABLE 2 - PHYSICAL PROPERTIES OF AN-Cu REACTION PRODUCTS

METAL WEIGHT %	APPEARANCE		MELTING POINT/°C	SPECTRAL
	PRODUCT	SOLUTION		
1. 10.28-o	ar: deep, pale blue wis: pale blue	w: pale blue a: pale blue	d 145-165	IR: nitrate UV: nitrate
2. 9.91-o	See above	See above	See above	See above
3. 10.13-c	ar: deep blue, green wis: green, brown	See above	d 140-160	See above
4. 39.75-o	ar: Cu, blue wis: Cu, green ppte	w: pale blue a: turquoise	AN: 160 AN+Cu: 158-160	See above
5. 39.87-o	ar: black, blue wis: black	See above	> 170	IR: oxide
6. 39.70-c	ar: deep blue wis: Cu, green	See above	100	IR: nitrate UV: nitrate

Legend: o-open environment
c-closed environment
ar-after reaction
wis-water insoluble
w-water
a-acid

TABLE 3 - POSSIBLE COPPER REACTION PRODUCTS

PRODUCT	APPEARANCE	SOLUBILITY	MELTING POINT/°C
Cu	Red	w: insoluble a: soluble -HNO_3, H_2SO_4 slightly soluble -HCl	1083
$Cu(NO_3)_2.3Cu(OH)_2$	Dark green	w: insoluble a: soluble	400(-H_2O)
$[Cu(NH_3)_n](NO_3)_2$ n = 2,4,5,6 $[Cu(NH_3)_4](NO_3)_2$	Blue	w: soluble	d 210
$Cu(OH)_2$	Blue	w: insoluble a: soluble	d (-H_2O)
$[Cu(H_2O)_n](NO_3)_2$ n = 3,6,9 $Cu(NO_3)_2.3H_2O$	Blue	w: soluble	114.5
CuO	Black	w: insoluble a: soluble	1326

TABLE 4 - AN TO COPPER MOLAR RATIOS

	BEFORE REACTION	AFTER REACTION
1.	6.9	5.7
2.	7.2	5.1
3.	7.0	8.5
4.	1.2	12.6
5.	1.2	2.7
6.	1.2	2.5

ZINC

Zinc and AN were reacted at metal weight percentages of 10, 15, 20 and 40 in both open and closed environments. The products were analyzed qualitatively (appearance, IR and UV spectra, melting point, and pH) and the results are given in Table 5. Table 6 is a list of possible reaction products. They were also analyzed quantitatively (weight, Kjeldahl, UV and AA) and the molar ratios of AN to Zinc are presented in Table 7.

NICKEL

Nickel and AN were reacted at metal weight percentages of 10, 20 and 40 in both open and closed environments. The reaction products were analyzed qualitatively (appearance, IR and UV spectra, and melting point) and the results are summarized in Table 8. The AN-Ni possible reaction products are listed in Table 9. Quantitative analyses (weight, Kjeldahl, UV and AA) were also conducted and the molar ratios of AN to Nickel are documented in Table 10.

CHROMIUM

The chromium-metal systems were at metal weight percentages of 5, 15 and 30 in both open and closed environments. The products were analyzed both qualitatively (appearance, IR and UV spectra, and melting points) and quantitatively (weight, Kjeldahl, nitron, and AA) and the results are summarized in Tables 11, 12 and 13.

TABLE 5 - PHYSICAL PROPERTIES OF AN-Zn REACTION PRODUCTS

METAL WEIGHT %	APPEARANCE		MELTING POINT/°C	SPECTRAL
	PRODUCT	SOLUTION		
1. 10.17-o	ar: Zn, white wis: grey(Zn) white ppte	w: clear a: clear	AN: 160 AN+Zn: 138	IR: nitrate UV: nitrate
2. 38.03-o	See above	See above	148	See above
3. 20.71-o	See above	See above	146	See above
4. 9.83-c	ar: white wis: white ppte	w: clear	d 110-120	See above
5. 19.94-c	ar: green, red white, grey wis: grey(Zn) white ppte	See above	green: d 190	IR: green-nitrate red-nitrate
6. 39.80-c	ar: pink, black wis: red, black, white ppte	w: clear a: clear	red: >200	IR: nitrate UV: nitrate metal-360-390nm
7. 9.90-o	ar: Zn, white wis: grey(Zn) white ppte	See above	AN: 163-165 AN+Zn: 138	IR: nitrate UV: nitrate
8. 14.23-o	ar: Zn, white wis: Zn, white ppte	See above	ar: 80-85 wis: >200	IR: ar-nitrate wis-oxide

Legend: o-open environment
c-closed environment
ar-after reaction
wis-water insoluble
w-water
a-acid

TABLE 5 - PHYSICAL PROPERTIES OF AN-Zn REACTION PRODUCTS (Cont'd)

METAL WEIGHT %	APPEARANCE		MELTING POINT/°C	SPECTRAL
	PRODUCT	SOLUTION		
9. 16.62-o	See above	See above	ar: 78-80 wis: >200	See above
10. 14.88-c	ar: white wis: white ppte	See above	ar: d 1500 wis: >200	See above
11. 9.95-c	See above	See above	ar: 134 wis: >200	See above
12. 18.78-c	ar: Zn, white wis: Zn	See above	AN: 160-162 AN+Zn: 148	See above

Legend: o-open environment
c-closed environment
ar-after reaction
wis-water insoluble
w-water
a-acid

TABLE 6 - POSSIBLE ZINC REACTION PRODUCTS

PRODUCT	APPEARANCE	SOLUBILITY	MELTING POINT/°C
Zn	Blue-white	w: insoluble a: soluble	419.4
$Zn(OH)_2$	Colourless	w: slightly soluble a: soluble	d 125
$Zn(NO_3)_2.3H_2O$	Colourless	w: soluble	45.5
$Zn(NO_3)_2.6H_2O$	Colourless	w: soluble	105-131 ($-6H_2O$)
ZnO	White, red green	w: insoluble a: soluble	1975
$Zn(NH_3)_n(NO_3)_2$ n = 2,3,4,6,8	---	---	---

TABLE 7 - AN TO ZINC MOLAR RATIOS

	BEFORE REACTION	AFTER REACTION
1.	7.2	19.2
2.	1.3	15.3
3.	3.1	14.8
4.	7.5	6.9
5.	3.3	3.5
6.	1.1	1.5
7.	7.4	36.8
8.	4.9	6.7
9.	4.1	6.7
10.	4.7	62.7
11.	7.4	98.9
12.	3.5	379.2

TABLE 8 - PHYSICAL PROPERTIES OF AN-Ni REACTION PRODUCTS

METAL WEIGHT %	APPEARANCE		MELTING POINT/°C	SPECTRAL
	PRODUCT	SOLUTION		
1. 10.46-o	ar: green, black wis: Ni	w: green a: clear	d 110-120	IR: nitrate UV: nitrate metal-378nm
2. 18.61-o	ar: green, black wis: Ni, green ppte	w: green a: green	See above	See above
3. 39.95-o	ar: green, black wis: grey	w: pale green a: deep green	d 190	See above
4. 9.94-c	ar: green, black wis: Ni, green ppte	w: blue-green a: pale green	d 120	See above
5. 20.02-c	See above	See above	d 100-110	See above
6. 40.66-c	ar: green, black wis: Ni	w: pale green a: deep green	See above	See above
7. −0.62-o	See above	w: blue-green a: clear	d 115-120	IR: nitrate UV: nitrate metal-390nm
8. 19.68-o	ar: Ni, green, black wis: Ni	w: blue-green a: pale green	d 110	See above

Legend: o-open environment
c-closed environment
ar-after reaction
wis-water insoluble
w-water
a-acid

TABLE 8 - PHYSICAL PROPERTIES OF AN-Ni REACTION PRODUCTS (Cont'd)

METAL WEIGHT %	APPEARANCE		MELTING POINT/°C	SPECTRAL
	PRODUCT	SOLUTION		
9. 11.06-c	ar: Ni, green wis: Ni, blue ppte	w: pale blue a: pale green	d 125	See above
10. 22.08-c	ar: green, black wis: Ni, green ppte	w: blue a: green	AN+Ni: 115-120 ppte: > 240	IR: nitrate ppte-oxide UV: nitrate

Legend: o-open environment
c-closed environment
ar-after reaction
wis-water insoluble
w-water
a-acid

TABLE 9 - POSSIBLE NICKEL REACTION PRODUCTS

PRODUCT	APPEARANCE	SOLUBILITY	MELTING POINT/°C
Ni	Silver	w: insoluble a: soluble- HNO_3, HCl, H_2SO_4	1453
$Ni(OH)_2$	Green	w: insoluble a: soluble	d 230
$[Ni(H_2O)_n](NO_3)_2$ n = 2,4,6,9 $Ni(NO_3)_2.6H_2O$	Green	w: soluble	56.7
$[Ni(NH_3)_n](NO_3)_2$ n = 1,2,6 $Ni(NH_3)_6(NO_3)_2$	Blue	w: soluble	---
NiO	Green-Black	w: insoluble a: soluble	1990
$[Ni(NH_3)_4(H_2O)_2](NO_3)_2$	Green	w: soluble	---

TABLE 10 - AN TO NICKEL MOLAR RATIOS

	BEFORE REACTION	AFTER REACTION	
		(a)	(b)
1.	6.3	4.1	5.6
2.	3.2	3.6	---
3.	1.1	3.7	5.0
4.	6.6	5.8	6.7
5.	2.9	4.4	---
6.	1.1	7.6	8.0
7.	6.2	4.1	5.0
8.	3.0	3.1	4.1
9.	5.9	5.6	5.7
10.	2.6	9.9	10.2

(a) calculation based on NH_3 content

(b) calculation based on NO_3^- content

TABLE 11 - PHYSICAL PROPERTIES OF AN-Cr REACTION PRODUCTS

METAL WEIGHT %	APPEARANCE		MELTING POINT/°C	SPECTRAL
	PRODUCT	SOLUTION		
1. 5.90-o	ar, wis, ais: grey	w: clear a: yellow	ar: >240	IR: --- UV: nitrate-256mn metal-350mn
2. 17.17-o	See above	w,a: yellow	ar: >240	See above
3. 29.78-o	See above	See above	ar: >240	See above
4. 14.28-c	ar: grey, white w,ais: grey	w,a: See above	ar: 150-160	IR: --- UV: nitrate-290nm metal-350nm
5. 4.94-c	ar: yellow, grey	w,a: See above	ar: 150-160	See above
6. 28.82-c	ar: black-grey w,ais: grey	w: deep yellow a: yellow	ar: >240	IR: --- UV: ---
7. 14.86-c	ar: black wis: grey ais: brown	w: deep yellow a: orange	---	See above
8. 5.66-c	ar: yellow, grey w,ais: grey	w: yellow a: pale yellow	ar: 75-80	IR: nitrate UV: nitrate-279nm metal-349nm
9. 28.91-c	ar,wis: grey ais: grey-black	w: pale yellow a: orange	ar: >200	IR: oxide UV: nitrate-292nm metal-344nm

Legend: o-open environment
c-closed environment
ar-after reaction
wis-water insoluble
w-water
a-acid

TABLE 12 - POSSIBLE CHROMIUM REACTION PRODUCTS

PRODUCT	APPEARANCE	SOLUBILITY	MELTING POINT/°C
Cr	Steel grey	w: insoluble a: soluble- H_2SO_4, HCl insoluble-HNO_3	1890
$Cr(OH)_2$	Yellow-brown	w: soluble a: soluble	---
CrO_2	Brown-black	w: insoluble a: soluble-HNO_3	300, -0
CrO	Black	w: insoluble a: insoluble-HNO_3	---
$[Cr(NH_3)_6](NO_3)_3$	---	---	---
$Cr(NO_3)_3.7½H_2O$	Brown	w: soluble	100

TABLE 13 - AN TO CHROMIUM MOLAR RATIOS

	BEFORE REACTION	AFTER REACTION	
		(a)	(b)
1.	10.4	170.1	---
2.	3.1	10.2	---
3.	1.5	76.2	---
4.	3.9	185.6	242.8
5.	12.5	142.3	145.9
6.	1.6	1.2	0.5
7.	3.7	0.9	0.6
8.	10.8	85.2	75.2
9.	1.6	209.0	180.9

(a) calculation based on NH_3 content

(b) calculation based on NO_3^- content

LEAD

Lead and AN were reacted at metal weight percentages of 20, 40 and 60 in both open and closed environments. Both qualitative (appearance, melting points, and IR and UV spectra) and quantitative (weight, Kjeldahl, nitron and lead sulphate precipitation, and AA) analyses were conducted. The results of these analyses are summarized in Tables 14, 15 and 16.

ALUMINUM AND IRON

These two elements were reacted with AN in a 10 percent (by weight) metal composition. As with the other elements, the reactions were conducted in both open and closed environments. There were no reaction products following the reaction. Iron may have oxidized to $Fe_2O_3 . x H_2O$ when the mixture was transferred into water, but it was apparent that neither iron nor aluminum had formed any type of metal salt derived from AN. It was concluded that these two elements are unreactive with AN in its solid state.

TABLE 14 - PHYSICAL PROPERTIES OF AN-Pb REACTION PRODUCTS

METAL WEIGHT %	APPEARANCE		MELTING POINT/°C	SPECTRAL
	PRODUCT	SOLUTION		
1. 20.35-o	ar: Pb, white wis: yellow-grey, white ppte	w: clear a: clear	AN: 157 AN+Pb: 100 wis: ppte: >220	IR: ar-nitrate wis-ppte-oxide UV: nitrate-306nm metal-340nm
2. 40.10-o	ar: Pb, white yellow wis: yellow-grey, white ppte	See above	yellow:>200 AN: 150-175 AN+Pb: 90-100 wis ppte: >200	See above
3. 59.21-o	ar: yellow, white wis: yellow-grey, white ppte	w: pale yellow a: clear	ar: >200 wis: ppte:>200	IR: ar-oxide wis ppte-oxide UV: nitrate-306nm metal-347nm
4. 21.61-c	ar: Pb, white NH_3 odour wis: yellow-grey, white ppte	w: clear a: clear	AN: 145-150 wis ppte: >220	IR: ar-nitrate wis ppte-oxide UV: nitrate-306nm metal-347nm
5. 41.59-c	See above	See above	AN: 135-140 wis ppte: >220	See above
6. 58.97-c	ar: yellow, white, NH_3 odour wis: white ppte	See above	ar: >200 wis ppte: >220	IR: ar-oxide wis ppte-oxide UV: nitrate-306nm metal-347nm

Legend: o-open environment
c-closed environment
ar-after reaction
wis-water insoluble
w-water
a-acid

TABLE 15 - POSSIBLE LEAD REACTION PRODUCTS

PRODUCT	APPEARANCE	SOLUBILITY	MELTING POINT/°C
Pb	Grey	w: insoluble a: soluble-HNO_3,H_2SO_4	327.5
$Pb(OH)_2$	White	w: insoluble a: soluble	d 145
$2PbO.H_2O$	White	w: insoluble a: soluble-CH_3COOH, HNO_3	d 145
$Pb(NO_3)_2$	Colourless	w: soluble	d 470
$Pb(OH)NO_3$	White	w: soluble	d 180
PbO	Yellow	w: insoluble a: soluble-HNO_3	888

TABLE 16 - AN TO LEAD MOLAR RATIOS

	BEFORE REACTION	AFTER REACTION	
		(a)	(b)
1.	21.4	22.4	13.7
2.	3.9	11.1	11.6
3.	1.8	0.4	1.5
4.	9.4	36.7	39.2
5.	3.6	23.1	22.8
6.	1.8	1.0	1.6

(a) calculation based on NH_3 content

(b) calculation based on NO_3^- content

DISCUSSION

The compositions of the reaction mixtures were such that there was an excess of AN at low metal percentages and an excess of metal at high metal percentages. When AN was in excess, it was difficult to analyze the reaction products since the excess AN and the resultant products were not readily separable. Also, when the reaction products were treated with water, it was very possible that the original salts hydrated - rendering the original product unrecoverable. Thus, for a more accurate analysis, an excess of metal would be preferred. The excess AN composition was retained, because in a real situation one will rarely encounter an excess of metal to AN in quantities large enough to pose a hazard.

It was found that AN started to decompose at a temperature below the melting point. As the temperature approaches the melting point, the rate of decomposition increases and subsequently the gaseous products could accelerate the decomposition. The presence of the metal further complicates the reaction system. The properties of the reaction products indicate that the AN and metal react in some way, but the mechanisms of the reactions are not known.

CONCLUSIONS

The reaction products of metal and ammonium nitrate under elevated temperature are complex mixtures of compounds. The formation of final products is influenced strongly by the confinement of the reaction system, the reaction temperature, the ratio of metal to ammonium nitrate and the granular size of the metal [1].

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APPENDIX 1 - KJELDAHL PROCEDURE AND CALCULATIONS

An aliquot containing approximately 2 milliequivalents of ammonia (25mL for 2 gram samples; 50mL for 1 gram samples) is pipetted into a Kjeldahl flask and diluted with 100mL of distilled water. Add a few anti-bumping granules. From a burette, dispense 50mL of standard HCl into the receiver (a 250mL beaker) and place it at the base of the condenser from the Kjeldahl apparatus. The tip of the condenser should be at least 1 cm below acid level to prevent any loss of ammonia during the distillation.

Add 3-4 grams of solid KOH to the contents of the Kjeldahl flask then immediately connect the flask to the distilling apparatus. Allow cold water to run through the condenser and heat the flask so that the contents boil gently. Continue the distillation for 30 to 40 minutes by which time all the ammonia should have distilled over into the receiver. Care should be taken not to let solution in the flask run dry. Remove heat and disconnect the Kjeldahl flask from the apparatus. Lower the receiver and rinse the condenser with distilled water. Add a few drops of methyl red indicator to the acid solution and titrate the excess with standard NaOH.

$$\%NH_3 = \frac{(NaVa - NbVb)}{v} \times \frac{V}{W} \times 80 \times 100$$

Where Na is the normality of the standard acid
Va, the volume of the standard acid in mL
Nb, the normality of standard base
Vb, the volume of the standard base in mL
V, the total volume of the sample in mL
v, the volume of the aliquot in mL
80, the molar mass of AN (in grams)
W, the weight of the sample in milligrams.

APPENDIX 2 - NITRON PROCEDURE AND CALCULATIONS

To prepare the reagent, one gram of nitron is dissolved in 10mL (or a proportionate amount) of 5% acetic acid. The solution is stored in a dark bottle as it does not keep well in the light.

The sample solution should contain 0.10 to 0.15 grams of nitrate. This solution is diluted to about 80mL with distilled water, acidified with 12 to 15 drops of 40% H_2SO_4, heated to boiling, mixed with 10 to 12mL of nitron solution, and allowed to stand for ½ to ¾ of an hour. The resulting crystals are aided in their growth by placing the solutions in an ice bath for one and one-half hour. The final batch of crystals are suction filtered on a Monroe or Gooch crucible under slight suction (with part of the filtrate used as the wash). The final wash is done using ice water (5 times 2mL portions). The precipitate is dried for 1 hour at 105°, allowed to cool and weighed.

$$\%\text{Nitrate} = \frac{Wn}{W} \times \frac{80}{375.2} \times \frac{V}{v} \times 100$$

Where Wn is the weight of the nitron precipitate in grams
W, the original weight of AN in grams
80, the molar mass of AN (in grams)
375.2, the molar mass of the precipitate (in grams)
V, the total volume of the sample in mL
v, the volume of the aliquot in mL.

APPENDIX 3 - LEAD SULPHATE PROCEDURE AND CALCULATIONS

The sample solution should contain 0.03 to 0.04 grams of lead. To this solution is added 10mL of concentrated H_2SO_4 and the mixture is heated until dense white fumes begin to evolve. From this point the solution is taken from the heat and diluted with distilled water to an acid concentration of 8%. The precipitate is filtered through a sintered glass crucible, washed with 6% H_2SO_4 (that has been saturated with $PbSO_4$), and dried for one hour at 600-800°C. Finally, when the crucibles are cool, they are weighed.

$$\% \text{ Pb} = \frac{Wls}{Wl} \times \frac{207.19}{303.25} \times \frac{V}{v} \times 100$$

Where Wls is the weight due to lead sulphate in grams
Wl, the weight due to the original lead in grams
207.19, the molar mass of lead (in grams)
303.25, the molar mass of lead sulphate (in grams)
V, the total volume of the sample in mL
v, the volume of the aliquot in mL.