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**HIGH ENERGY OXIDIZER
STABILIZATION STUDIES (U)**

**FINAL REPORT
TECHNICAL REPORT AFRPL-TR-66-145
JULY, 1966**

373914

Sponsored By
Air Force Rocket Propulsion Laboratory
Research and Technology Division
Air Force System Command
Edwards, California

James E. Coleman
Esso Research & Engineering Company
Linden, New Jersey

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⑥ **HIGH ENERGY OXIDIZER STABILIZATION STUDIES (U).** ⑧

⑨ Final rept. 14 Jan 65-14 May 66,

⑩ James E. Coleman,
Esso Research & Engineering Company
Linden, New Jersey

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FOREWORD

This report describes research aimed at stabilization of nitronium perchlorate (NP) via the use of additives, new treatment procedures and new synthesis techniques. The research was sponsored by the Air Force Systems Command, U. S. Air Force, Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards Air Force Base, California (93523) under contract No. AF-04 (611)-10538. The program was administered by Mr. J. L. Trout, Project Engineer, Air Force Flight Test Center, Edwards Air Force Base, California. The research was initiated on January 14, 1965 and this report covers the period January 14, 1965 to May 14, 1967. The report was submitted on June 14, 1967.

The following technical personnel contributed to this research:

Dr. J. E. Coleman (Principal Investigator)
Mr. E. J. Lucker (Investigator)
Mr. P. L. Gerhardt (Analytical Research)
Mr. G. G. Wanless (Analytical Research)

The project was under the general administration of Dr. J. R. Lovett, Assistant Director and Dr. T. J. Wallace, Group Leader.

This report contains material extracted from confidential documents which are listed in the reference section.

This technical report has been reviewed and is approved.

George F. Babits
Lt. Colonel, USAF
Chief, Propellant Division

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UNCLASSIFIED ABSTRACT

Stabilization studies on a higher energy oxidizer included the study of the early stages of thermal decomposition, analysis of a contaminate, optimization of a treatment procedure, studies on the mechanism of stabilization and a semi-empirical additive screening study. Decomposition studies showed that changes in the decomposition process occurred during early stages of decomposition. Gas evolution during the induction period is unrelated to the length of the induction period. A new method of stabilization was demonstrated and optimized. Attempts were made to overcome the inherent disadvantages of the stabilizer. A synthesis study indicated that synthesis conditions affect the stability of the oxidizer. Leads on new additives were found in the screening study.

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I. INTRODUCTION

(C) Nitronium Perchlorate (NP) is the most energetic solid oxygen oxidizer known. Many of the properties of NP enhance its potential as a solid propellant ingredient. In addition to its high energy value, it is a non-volatile, high melting, dense crystalline solid which can be prepared easily at a reasonable price and handled safely on a large scale. Only its extreme reactivity and marginal thermal stability have prevented its utilization in solid propellant formulations.

A. OBJECTIVES OF THE PRESENT STUDY

(C) This study focused on the problem of NP's thermal stability. The overall purpose of the study was to discover methods of preparing stabilized NP either by the use of additives, new heating techniques, and by new synthesis techniques from ultra-pure raw materials. The primary objective was the preparation of NP which shows no gas evolution at 60°C for 100 hrs. In addition to this primary goal, we realized that the ultimate use of NP is also dependent on its long-term stability. Since the decomposition of NP has been characterized as an autocatalytic process, the start of the accelerated decomposition is critical to its long-term stability. Therefore, a secondary objective of the study was the discovery of factors which inhibit or retard the onset of the accelerated decomposition.

B. TECHNICAL BACKGROUND

1. Nature of the Problem

(U) The thermal decomposition of nitronium perchlorate has been studied (1) in the range of 69.99 to 112.3°C. This kinetic study of the overall decomposition revealed that (1) the decomposition is an autocatalytic process; (2) there is an induction period with a slow, nearly constant gas evolution (corresponding to 0.5% decomposition); (3) except for minor changes in the induction period, there is no variation with sample size; (4) the decomposition gives approximately 3 moles of gas per mole decomposed; (5) the maximum rate occurs when the fraction decomposed (α) is approximately 0.2; (6) during the acceleration period, α is proportional to t^4 ; and (7) after the maximum, $d\alpha/dt$ shows a linear decrease with increasing α . It was found that between 0.5 to 95% decomposition, the data agreed with the theory of Mampel. Thus, after the induction period, the process consists of a first-order initiation of nuclei followed by three-dimensional growth of these nuclei. A suggested modification of the theory included a mobile equilibrium of the active sites and the interpretation that the particle size referred to a sub-crystalline unit.

(U) The overall decomposition of NP serves as a reference point in the study of its stabilization. The autocatalytic decomposition is typical of exothermic solid decompositions (2) which give a characteristic sigmoid curve shown in Figure 1. However, our interest lies in the very early stages of decomposition which is noted by the small rectangle in Figure 1. This area is magnified in Figure 2.

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Figure 1

Typical Decomposition Curve (U)

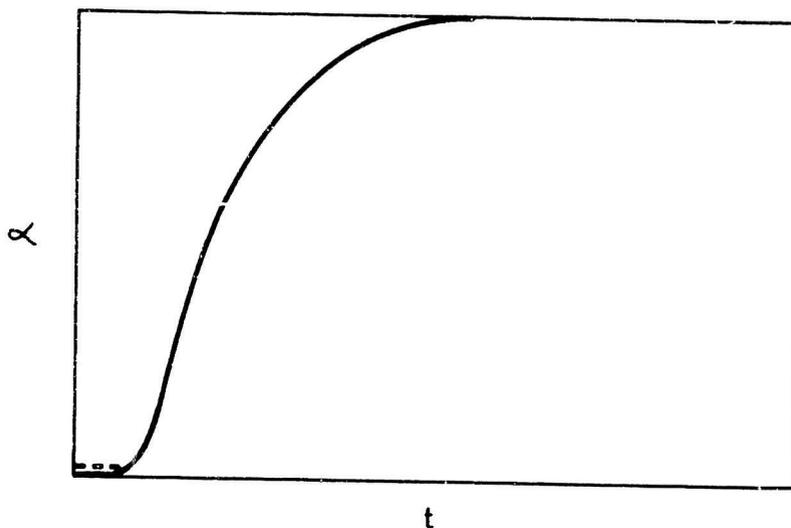
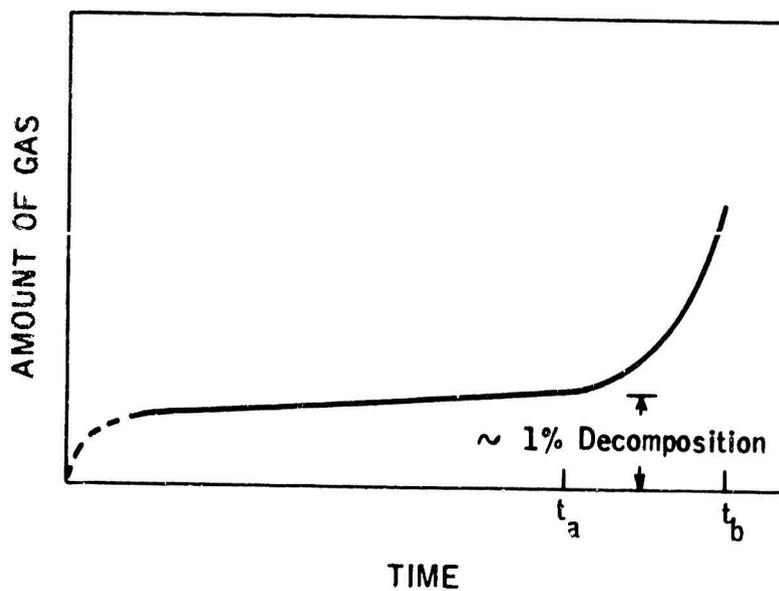


Figure 2

Initial Decomposition Curve (U)



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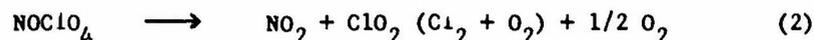
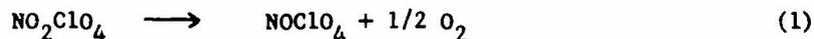
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a. Two Problems Exist

(U) From Figure 2 it is evident that the stability of NP actually involves two problems. The first is the retardation of the onset of the accelerated reaction (t_a). In any practical use of NP as a propellant, the autocatalytic decomposition represents a severe hazard which must be avoided during the life time of the propellant. Thus, large values of t_a are necessary. The second problem is the minimization of the gas evolution during the induction period. Gas evolution during formulation and storage leads to voids in the propellant which cause burning difficulties. In addition, the use of coatings to overcome the high reactivity of NP requires minimal gassing to avoid rupture of the coating. Experience with other decompositions of this type (2) indicates that these two are probably unrelated.

b. Study Restricted to First Percent of Decomposition

(C) Another point that is evident from the figures is that stabilization is related to factors affecting the first percent of the decomposition. In addition to the difficulties inherent in studying such small changes, there is the added complication that the early stages of decomposition are different from the overall process. Callery (3) has shown that the decomposition can be represented by the following equations:



During the early part of the acceleration, reaction 1 is the predominant reaction. At some point (t_b), which is not evident from the gas evolution curve, reaction 2 becomes important. The overall reaction produces 3 moles of gas per mole of NP decomposed. However, during the initial acceleration, only 0.5 mole of gas is produced per mole decomposed. Thus, the 0.5% decomposition reported for the lower limit of agreement with theory may represent up to 3% of actual decomposition. The 1% decomposition shown in Figure 2 is based on reaction 1. Lack of knowledge of both the processes involved in the induction period and the composition of the gas evolved in this period provide further incentive for the study of this period.

2. Previous Findings

(U) Previous work on the stabilization of NP was carried out at Esso under ARPA Contract No. DA-30-069-ORU-74. Since the current study is an extension of this earlier work, the highlights of this work are summarized below. In considering the previous data, it is important to realize that the measure of stability was the amount of gas evolved in unit time at a given temperature. The importance of t_a was realized just prior to the current study.

a. Water Affects Stability of NP

(C) The previous results obtained by Esso and others supported the view that environmental water is detrimental to NP (4). This hypothesis was largely based on the fact that the stability of commercial NP (Callery) could be improved by vacuum drying or by storage in a dry-box with a moisture content of only 1 to 5 ppm. In order to test this hypothesis, a proton analysis method was developed, but the final testing was done under the current study.

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Stability Variation with Water Content of Environment (0.1 g. samples)

| <u>Water Content of Environment, ppm</u> | <u>Test Temp. °C</u> | <u>Gas Evolved std. cc./g./100 hrs.</u> |
|--|----------------------|---|
| 50-100 | 40 | 6.6 |
| ~ 5 | 40 | 0.4 |
| ~ 5 | 60 | 4.0 |
| < 1 | 60 | 1 to 3 |

The above data indicated that environmental water is detrimental to the stability of NP. However, the current study showed that the relationship between water and NP stability is more complicated than indicated by this conclusion.

b. BF₃ Improves NP Stability

(C) Initial screening studies on NP stabilization showed that BF₃ has a significant stabilizing effect. This initial finding was based on contacting "as received" NP with BF₃. This treatment was subsequently found to be equivalent to drying. Repeated treatment or combined treatment of drying and BF₃ contacting had little effect. However, when a small BF₃ pressure was left over the sample, further stabilization was noted.

| <u>Sample (0.1 g.)</u> | <u>Std. cc./g./100 hrs. at 60°C</u> |
|-----------------------------|-------------------------------------|
| Dried NP | 2 to 3 |
| NP + 10 mm. BF ₃ | 0.6 |

c. Test Conditions Influence Stability Results

(C) During the previous study, we discovered that other variations in test conditions gave unexpected variations in results (5). The most dramatic effect was the importance of the sample weight/test volume ratio. As this ratio is increased, the apparent stability of NP also increases as illustrated by the following data.

Variation of Apparent Stability with Sample Size 10 cc. test volume

| <u>Sample Size g.</u> | <u>Evolved Gas, std. cc./g./100 hrs.</u> | | |
|-----------------------|--|--------------------|-------------|
| | <u>60°C</u> | <u>70°C</u> | <u>75°C</u> |
| 0.1 | 1.2 to 5.1 (3.5 ± 0.5 most freq.) | 2.0, 3.6, 3.1, 3.1 | ---- |
| 0.5 | 0.4 to 1.0 | 0.80, 0.65 | ---- |
| 1.0 | 0.3 to .5 | 0.39, 0.39 | 1.34 |
| 2.0 | ---- | ---- | 0.65 |

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Variation of Apparent Stability with Test Volume

(0.5 g. Samples)

| <u>Test Volume, cc.</u> | <u>Gas Evolved, std. cc./g./100 hrs. at 60°C</u> |
|-------------------------|--|
| 5 | 0.37, 0.67 |
| 10 | 0.82, 0.82, 0.96 |

In addition, there is some evidence that other factors also produce minor variations in apparent stabilities. These factors include the use of mercury monometers for measuring pressure, the procedures for cleaning the test apparatus, and possibly, reaction with the glass surface. However, experimental error makes it difficult to assess the effect of these variables with any degree of certainty.

3. General Approach

a. Test Method Selected

(U) Since the limited knowledge was available on the induction period, indicated experimental error, unresolved dependence on test conditions, and anticipated screening studies, we realized that a large number of stability tests would be necessary in this study. Therefore, the basic test method selected for these studies was the standard Vacuum Thermal Stability (VTS) test used in previous work. This test and others developed in the current study are described in Appendix I. Although this method had several minor disadvantages, e.g., reaction of the product gases with the mercury in the manometer, this was overshadowed by (1) the simplicity of the test; (2) the number of tests that could be carried out simultaneously; and (3) lack of any other trouble-free method. In addition, tests were largely restricted to 0.5 g. samples since we were more interested in inherent stability factors rather than test parameter effects. A further restriction was the almost exclusive use of 60°C as a test temperature which is specified in the target goal.

b. Proton Analysis Used as a Guide

(C) In order to verify the effect of water on the stability of NP, some measure of the "water" content was required. We used the proton analysis technique developed under the ARPA contract to correlate the "water" content with stability. In this correlation, we investigated both the initial gas evolution and the time to the onset of the accelerated decomposition, t_a .

c. Stabilization Study Designed to Aid Additive Selection

(C) Initially, a basic study of BF_3 stabilization was planned. In this study we hoped to determine (1) the effect of BF_3 on the nature of the NP decomposition, (2) the stoichiometry of BF_3 stabilization, and (3) the nature of the interaction of BF_3 with NP. Later, this approach was shifted to a more promising additive. In these studies, we hoped to establish a basis for the future selection of additives for NP stabilization. For effective additives, maximum stabilization was established by optimization studies. In addition to this fundamental approach, we continued some limited, empirical screening studies.

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d. Ultra-Pure NP to be Synthesized

(U) Although our major effort was directed toward the stabilization of commercial NP, synthesis of ultra-pure NP was planned. Use of an available, small laboratory synthesis unit was expected to provide the preparation of ultra-dry NP and also evaluation of purity variation with synthesis conditions. Comparison of the stability of NP prepared in the laboratory with that of commercial NP would give further insight into the need for stabilization of the latter. However, severe limitations to this approach were uncovered in the course of our studies.

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II. SUMMARY

(U) Stabilization of nitronium perchlorate (NP) was approached by a study of its early decomposition, a mechanism study on known stabilizers, and an empirical screening study of various additives. Stability measurements were based on a 60°C Vacuum Thermal Stability (VTS) test. Two criteria of stability were observed -- (1) gas evolution after 100 hrs. at 60°C, and (2) the time for the onset of accelerated decomposition (t_a). Decomposition studies showed that NP gives widely scattered results; that the decomposition process undergoes change between each of the three periods: induction, early acceleration, and late acceleration.

(C) Stabilization by boron trifluoride (BF_3) is of limited utility. For some samples, contacting with BF_3 is equivalent to drying and results in lower gas evolution. For other samples, contacting with BF_3 has little if any effect. Stability tests run in the presence of BF_3 indicate lower gas evolution but BF_3 is consumed. Mass spectral results indicate that BF_3 scavenges nitrogen oxides. Moderate pressures of BF_3 (ca. 600 mm) appear to increase t_a but the effect is not large.

(C) A study of the proton content of various NP samples showed a complex relationship between NP stability and water. NP is hygroscopic and readily reacts with H_2O ; however, volatile products are formed and therefore the "water" can be removed. This relationship appears to be responsible for the wide variation in stability results. At low levels of water, gas evolution appears to increase with increasing water content; but, optimum amounts of water retard the onset of accelerated decomposition. However, the history of the sample can be as important as the "water" content.

(C) Water treatment of NP produces a marked increase in t_a . Untreated NP undergoes accelerated decomposition after 100 hrs. In contrast, NP treated with 1.23 wt. % H_2O (10 mole %) has produced values of t_a greater than 1000 hrs. at 60°C. In addition, this treatment gives minimal gas evolution (0.5 std. cc./g./100 hrs.) for treatments in the range of 5 to 15 mole % H_2O . A study of variables showed that treatment procedures are important. Also the stabilization of water treatment can be reversed by pumping.

(C) Other studies indicate that the stabilizer in water-treated NP is hygroscopic nitronium perchlorate, $H_2NO_2(ClO_4)_2$, which actually is a mixed crystal system of hygroscopic perchlorate and NP. This implies that stabilization is effected by modification of the crystal structure of the surface layers of NP.

(C) Because of the "reversibility" of water treatment, maintenance of NP stability requires coating. Unfortunately water-treated NP has sufficient volatility to interfere with the "Reta" coating process. Attempts to control this volatility included precoating with Kel-F waxes and ammonia treating. Pellets made from 10 mole % water-treated NP were precoated with Kel-F waxes. Some reduction in volatility was obtained; but, the films of Kel-F wax were too weak to give complete retention of the stabilizer. Ammonia treatment of water-treated NP also reduces the volatility. However, a short study of the effect of treatment conditions showed wide variations. These results indicate very complex interactions; thus, it is doubtful the process can be utilized.

(C) The additive screening study indicates that few materials improve the stability of NP. The results showed some improvement by fluorine, iodine pentoxide, and some acids. The latter is probably a variation of water treatment. The first two do not appear practical but may merit further study from a mechanism standpoint. Many other materials such as salts, metal oxides, fuels and others are detrimental to the stability of NP.

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(C) We attempted to modify the crystal surface of NP with nitronium and ammonium tetrafluoroborate. However, these attempts did not show any signs of improved stability. Lack of a good solvent for intimate mixing seriously jeopardized this approach.

(C) NP was prepared in a laboratory unit designed to produce ultra-dry and CO₂-free NP. Complete elimination of CO₂ was not achieved. All samples showed high gas evolution; but, we believe this is due to the very small particle size produced rather than the presence of impurities.

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III. GENERAL STUDY OF INITIAL DECOMPOSITION

A. RESULTS SHOW VARIATIONS

(U) Stability results on NP from various laboratories showed a wide range of values. From our previous work, the obvious explanation for this result was variation in environmental factors. However, multiple tests were undertaken to demonstrate the reproducibility of results obtained in our laboratory. Surprisingly, our results showed considerable variation.

1. Stability Results Show Marked Scatter

(C) As mentioned in the introduction, our prime measures of stability are the total gas evolution per gram of NP after 100 hrs. at 60°C in the standard test procedure (Appendix I) and the time for the onset of the accelerated decomposition (t_a). Multiple tests were made using NP from two different bottles of NP. The designation of these samples is summarized below:

| <u>Our Designation</u> | <u>General Reference</u> | <u>Callery Lot No.</u> |
|------------------------|--------------------------|------------------------|
| 276-6 | Older Callery Bottle | 1293-10 |
| 276-138 | Newer Callery Bottle | 1293-10-28 |

The results of these tests showed considerable scatter in gas evolution and an apparent difference in the two samples.

| <u>NP Bottle</u> | <u>Number of Samples in Various Thermal Stability Groups</u> | | | | | |
|------------------|---|----------------|----------------|----------------|----------------|--------------|
| | <u>Groups Based on cc. of gas evolved/g./100 hrs. at 60°C</u> | | | | | |
| | <u>0-0.20</u> | <u>.21-.40</u> | <u>.41-.60</u> | <u>.61-.80</u> | <u>.81-1.0</u> | <u>1.01+</u> |
| 276-6 | --- | 2 | 6 | 2 | 2 | --- |
| 276-138 | --- | 2 | 3 | 6 | 2 | --- |

In contrast, the t_a results showed only minor scatter for bottle 276-6 but considerable scatter for bottle 276-138. This latter effect may have been related to the freshness of the sample.

| <u>NP Bottle</u> | <u>Number of Samples in Various Acceleration Groups</u> | | | | | | |
|------------------|--|---------------|----------------|----------------|----------------|----------------|-------------|
| | <u>Groups based on time to onset of acceleration, hrs.</u> | | | | | | |
| | <u>0-50</u> | <u>51-100</u> | <u>101-150</u> | <u>151-200</u> | <u>201-300</u> | <u>301-400</u> | <u>400+</u> |
| 276-6 | --- | 10 | 1 | 1 | --- | --- | --- |
| 276-138 | --- | 3 | 2 | --- | 2 | --- | 4 |

This scatter was too large to be attributed to experimental error. Thus, the initial stages of the decomposition appeared to be sensitive to parameters not normally considered as variables. Later work confirmed this conclusion.

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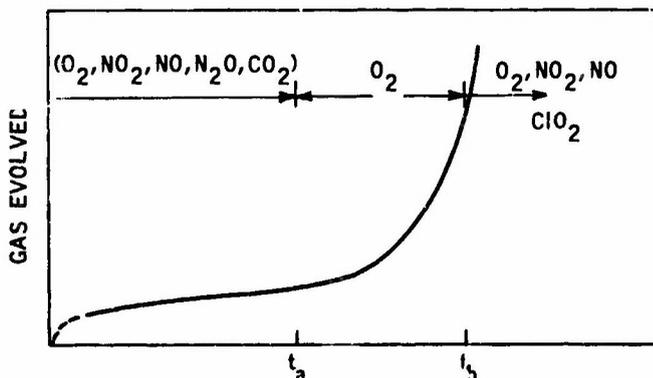
10

2. Gas Product Distribution Varies During Decomposition

(C) Mass spectral analysis was carried out on the gases from a series of decomposition runs to increase our knowledge of the induction period. In this series of runs, sealed tubes without manometers were used to avoid modification of the gas by reaction with mercury. It was hoped that the composition of the evolved gases would provide some insight on the processes by which they arise. The following graph summarized the main variation in composition of the gas evolved during the initial stages of decomposition.

Figure 3

Variation of Gases Evolved (U)



4. Many Gases Evolved During Induction Period

(C) The mass spectral analysis of the gas evolved during the induction period indicated that the mixture consisted of O_2 , NO_2 , NO , CO , N_2O , HCl , ClO_2 , H_2O and N_2 . The most predominant gases were O_2 , NO_2 , NO , N_2O and CO_2 . The presence of CO_2 presents a problem which is discussed in detail below. Since the acceleration stage apparently arises from the growth of $NOClO_4$ nuclei, the evolution of oxygen during the formation of the nuclei is expected. The apparent presence of nitrogen oxides suggested some alternate process was also operating during this period. However, the mass spectral analysis is subject to error if nitric acid is present.

(U) In order to determine the limitations of the mass spectral analysis, 100% nitric acid was analysed. The following results were obtained.

| <u>Run No.</u> | <u>% O_2</u> | <u>% CO_2</u> | <u>% N_2</u> | <u>% H_2O</u> | <u>% NO_2</u> | <u>% NO</u> | <u>% N_2O</u> |
|----------------|---------------------------|----------------------------|---------------------------|----------------------------|----------------------------|--------------------------|----------------------------|
| 1 | 0 | 0 | 0 | 58 | 8.1 | 13.0 | 6.0 |
| 3 | 1.4 | 0 | 1.1 | 16.9 | 16.9 | 0 | 5.4 |

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As shown, our mass spectral analysis cannot distinguish between HNO_3 and the nitrogen oxides. Furthermore, the variations in response makes it impossible to correct for possible HNO_3 contribution. The suspected contamination of NP by water is a likely source of HNO_3 .



In addition, pressure measurements on the product gases at different temperatures show deviations from ideality. This suggests that condensable gas is present. Thus, HNO_3 is the most likely source of the nitrogen oxides indicated by the analysis.

b. Oxygen Evolved During Early Acceleration Stage

(C) For runs stopped in the early part of the acceleration stage, the mass spectral analysis showed a similar composition but a much higher O_2 content. Consideration of the relative amounts of gas evolved during the two stages led us to conclude that only O_2 was liberated in the early stages of the acceleration process. This result confirms the earlier conclusions of Callery.

c. NO_2 Evaluation Delayed in Acceleration Stage

(C) The build-up of NOClO_4 during the early stages of accelerated decomposition finally results in the formation of NO_2 which is readily detected by its characteristic reddish-brown color. From our results, gas evolution of the order of 3 to 4 std. cc./g. of NP (approximately 4% decomposition) and higher were obtained before NO_2 was detected. Mass spectral data also indicated that little evolution of nitrogen oxides occurred prior to the appearance of the characteristic color of NO_2 .

B. PRESENCE OF CO_2 NOT UNDERSTOOD

(U) The presence of CO_2 in the gases evolved during the induction period was unexpected but its presence was confirmed by gas chromatography. The mass spectral analysis indicated that it was present in about 20 to 40%. Thus, this is a significant contribution to the gases evolved during this period.

1. Source of CO_2 Unknown

(U) Even though the CO_2 represents a significant portion of the decomposition products of the induction period, it presents less than 1% carbon in the NP. The most likely sources of the CO_2 are (1) a carbonaceous impurity in the NP, (2) carbonaceous impurities on the test equipment, and (3) adsorbed CO_2 . Although the source of this CO_2 is still unknown, it is doubtful that it arises from the test equipment. The sealed glass tubes were flamed prior to use. In addition, the analysis of 100% nitric acid gave no indication of CO_2 ; thus, it does not arise from the analytical equipment.

2. CO_2 Problem Not Fully Resolved

(C) Since the elimination of CO_2 from the product gases should significantly reduce the gas evolution during the induction period, several attempts were made to reduce this gas. CO_2 adsorbed during synthesis seemed to be a likely source of the gas. Although attempts to measure the adsorption of CO_2 on NP at room temperature gave no detectable adsorption, the gas evolution during stability testing was greater after the NP had been

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in contact with CO₂. However, NP synthesized in CO₂-free air (Section X) also evolved CO₂. In conjunction with our studies on water-treated NP (described in Section VI), attempts were made to eliminate CO₂ by heat treatment. The rationale for this approach was that CO₂ is probably released during the initial heating of the sample and removal of gases at this stage would eliminate any further contributions from CO₂. These attempts, however, resulted in increased gas evolution and this approach was therefore dropped.

| <u>Treatment</u> | <u>Gas Evolution, std. cc./g./100 hrs. at 60°C</u> |
|--|--|
| 10 mole % H ₂ O-treated NP | 0.40 to 0.60 |
| Heated 22 hours at 60°C then 10% mole % water-treated | 1.20 |
| 10 mole % H ₂ O-treated NP heated 6 hours at 60°C then evacuated | 1.5 |

(U) The incentive for CO₂ elimination, which is a marginal improvement in gas evolution during the induction period, still remains. Further work on this problem was deferred because of the more important need for control of t_a .

C. MERCURY MODIFIES TEST RESULTS

(U) The possible influence of mercury on the decomposition of NP was investigated. The initial test results, shown below, indicated that mercury produces two effects on the results. The amount of initial gas evolved appears to be decreased by reaction of the product gases with the mercury. This was based on the condition of the mercury in the manometer. The magnitude of this effect appears minor. The second effect is an apparent mercury catalyzed decomposition of NP brought about by vapor transfer from the manometer to the NP. The addition of mercury to the sample is obviously detrimental. However, later work with stabilized NP showed that mercury has no effect on the start of the acceleration reaction.

Effect of Mercury on 60°C Stability

| <u>Test Condition</u> | <u>Std. cc./g./100 hra.</u> | <u>t_a, hra.</u> |
|---|-----------------------------|-------------------------------|
| Standard VTS (Hg vapor present) | 0.1 to 0.80 | 70-150 |
| Valve in manometer (Hg vapor exposure limited) | 0.81 to 1.00 | 201 to 400 |
| Mercury added (Liquid Hg-solid NP contact) | 1.21 to 1.4+ | 50 to 100 |

Time to Formation of Brown Fumes

| <u>Test Condition</u> | <u>Hours</u> |
|-----------------------|--------------|
| Standard VTS | <200 |
| Sealed tube, no Hg | 222 to 412 |

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IV. BORON TRIFLUORIDE STABILIZATION

A. BORON TRIFLUORIDE IMPROVES STABILITY RESULTS

(C) As mentioned in the Introduction, previous studies showed that some stabilization of NP could be effected by treatment with boron trifluoride. However, the effect appeared to be limited. In the present study, we hoped that a further investigation of BF_3 stabilization would provide us with some insight for the selection of better additives.

1. Boron Trifluoride Lowers Gas Evolution Results

(C) The effect of BF_3 varied with different samples of NP. The earlier work indicated that lowering of gas evolution of some samples was apparently the result of drying. The effect on "dry" samples of NP was dependent on the presence of BF_3 during the stability test. The table below summarizes some of our stability results in the presence of BF_3 .

| <u>Treatment*</u> | <u>Std. cc./g./100 hrs. at 60°C</u> | <u>t_a, hrs.</u> |
|--|-------------------------------------|----------------------------|
| 20 mm. argon | 0.28, 0.36 | 90 |
| 43 mm. argon | 0.40, 0.50 | 130 |
| (10 to 14 mm. BF_3 then evacuated)-Repeated 3 times | 0.52 to 0.56 | 60 to 90 |
| 12 mm. BF_3 | 0.24, 0.30 | 90 |
| 14 mm. BF_3 | 0.10, 0.06 | 100, 110 |

* NP used was a homogenized sample from bottle 276-138.

The gas evolution from the evacuated sample is within the range noted for the untreated sample (Section III, A). A comparison of the argon and BF_3 results indicates that the effect of BF_3 is chemical in nature and not related to pressure. The variations in t_a are probably due to experimental error.

2. Boron Trifluoride Retards Acceleration Slightly

(C) The scatter in the t_a values among the lower pressure BF_3 -treated and untreated NP stability tests suggested that any effect of BF_3 on t_a was overwhelmed by some other factor which is not readily controlled in duplicate tests. To determine if BF_3 did effect t_a, tests were conducted at higher pressures. These experiments were carried out in sealed tubes without manometers. The occurrence of accelerated decomposition was determined by the formation of brown fumes. Thus, these tests actually refer to t_b (time for the formation of NO_2) but should reflect changes in t_a (see Figure 2).

Time to Formation of Brown Fumes

| <u>Test Condition</u> | <u>t_b, hours</u> |
|------------------------------------|-----------------------------|
| Sealed tube, no BF_3 | 222, 364, 388, 412 |
| Sealed tube, 100 mm. BF_3 | 388, 517 |
| Sealed tube, 760 mm. BF_3 | 607, 607 |

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The sealed tube results in the absence of BF_3 show the magnitude of the effect of the unknown factor on t_a . The BF_3 results show a minor increase in t_b . Thus, the data suggest that BF_3 tends to enhance t_a , but other factor(s) are more important.

B. BF_3 CONSUMED DURING STABILIZATION

(C) VTS tests were run on NP samples initially treated with BF_3 . Mass spectral analysis of the evolved gas showed that BF_3 was not present. Thus, BF_3 is consumed during the decomposition. For the low pressure (12 mm.), the consumption of BF_3 causes an error of up to 0.2 to 0.4 std. cc./g. in the results. Thus, BF_3 stabilization is not as good as the data indicate. Other mass spectral data were obtained in sealed tube experiments (no mercury present) after 48 hours at 60°C. These data gave the product distribution shown below.

| Sample | Gas Product Distribution After 48 Hours at 60°C | | |
|--|---|--------------------------|--------------------------|
| | NO_2/O_2 | NO/O_2^* | CO_2/O_2 |
| 276-138-54** | 1.47 | 0.85 | .86 |
| 276-138-54 | 0.99 | .61 | .86 |
| 276-138-54 plus BF_3 treating | 0.14 | .10 | .60 |

* At the low pressures involved, the reaction $\text{NO} + 1/2 \text{O}_2 \longrightarrow \text{NO}_2$ is slow and NO and O_2 exist together for days.

** Homogenized sample from bottle 276-138.

The variation in the first two runs is typical of other mass spectral results on NP decomposition gases. This variation is further evidence that the contribution of nitrogen oxides to the gas evolution during the induction period is related to impurities rather than the decomposition of NP per se. The similarity of the CO_2/O_2 ratios indicates that acceleration has not occurred; therefore, none of the results are influenced by large O_2 evolution. The reduction in the nitrogen oxides after BF_3 treatment indicates reaction with nitrogen oxides or their precursors. Such reaction would yield NO_2BF_4 and/or NOBF_4 (6) plus other products. Although independent processes for the stabilization of NP and the consumption of NP cannot be excluded, BF_3 appears to be a scavenger of nitrogen oxides.

C. BF_3 STABILIZATION NOT ENCOURAGING

(C) In view of the effect of BF_3 on gas evolution and t_a , it seems reasonable to conclude that the stability imparted by this reagent is less than that suggested by our original data. The lowering of the gas evolution may only be an artifact of its consumption. Furthermore, other methods are more effective for increasing t_a . This became apparent in the work that led to water treatment of NP. During this development, a sample which originated from bottle 276-6 was inadvertently exposed to moisture. This sample of "wet 276-6" (0.043 wt. % H) proved to be fairly stable against accelerated decomposition. BF_3 treatment of this sample showed lower gas evolution.

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BF₃ Stabilization of "Wet 276-6"

| <u>Treatment</u> | <u>std. cc./g. at 60°C</u> | | <u>t_a, hrs.*</u> |
|---|----------------------------|-----------------|-----------------------------|
| | <u>100 hrs.</u> | <u>400 hrs.</u> | |
| Untreated | .8 to 1.12 | 2.18 to 3.38 | > 600 |
| Evac. 23°, 10 mm. BF ₃ , evac. 28°C | .62 | 1.2 | > 550 |
| Evac. 28°, 10 mm. BF ₃ , evac. -196°C | .60 | 1.18 | > 550 |
| Evac. -196°C, 10 mm. BF ₃ , evac. -196°C | .72 | 3.0 | 150 |
| Evac. 28°, 10 mm. BF ₃ | .42 | .82 | > 550 |

* Runs with greater than signs terminated without acceleration.

Although variations in the test procedures appear to effect the results, the wet sample gives higher values of t_a than the original. In this case, the lowering of the gas evolution by BF₃-treatment appears real. The treatment is effective even when the BF₃ is removed by evacuation. However, further work on H₂O-treatment (Section VI) showed that 10 mole % H₂O is the optimum level of treatment. NP so treated is not improved by addition of BF₃.

BF₃ Treatment of 10 mole % H₂O-Treated NP

| <u>BF₃ Treatment</u> | <u>std. cc./g. at 60°C</u> | | <u>t_a, hrs.</u> |
|---|----------------------------|-----------------|----------------------------|
| | <u>100 hrs.</u> | <u>400 hrs.</u> | |
| No BF ₃ treatment | .4 to .58 | .74 to 1.43 | > 690 |
| Evac. 28°C, 9 mm. BF ₃ , evac. | .46 | 1.10 | > 630 |
| Evac. -196°C, 9 mm. BF ₃ , evac. | .54 | 1.44 | 400 |
| Evac. 28°, 9 mm. BF ₃ | .52 | 1.12 | > 630 |
| Evac. -196°C, 9 mm. BF ₃ | .56 | 1.44 | 400 |

Further, one combined treatment consisted of adding BF₃ to the H₂O-treating vessel at the end of the 10 mole % H₂O-treatment. The BF₃ was then removed by pumping at -80°C. This material was no better than our best water-treated NP.

| <u>Sample</u> | <u>Evac. Temp.</u> | <u>std. cc./g. at 60°C</u> | | <u>t_a</u> |
|--|--------------------|----------------------------|-----------------|----------------------|
| | | <u>100 hrs.</u> | <u>400 hrs.</u> | |
| BF ₃ treated 10 mole % H ₂ O-treated | -196°C | 0.40 | .90 | > 550 |
| | 28°C | 0.38 | .86 | > 980 |

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(C) From these studies, it was apparent that BF_3 treatment is of limited utility.* It was also evident that other factors, notably water treatment, have a greater effect on NP stability. Finally, the wide variation in experimental results made further mechanism studies virtually impossible. Thus, studies on BF_3 stabilization were terminated and water treatment, which appeared to be more promising, was pursued instead.

*Note: Although the results here show BF_3 to be of limited use, it should be noted that the application of BF_3 treatment in conjunction with Reta coating has shown significant lowering of the initial gassing (7).

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V. RELATIONSHIP OF WATER CONTENT TO STABILITY

(C) Originally, we thought that ultra-dry NP was the key to stability. In order to demonstrate this, a proton analysis method (Appendix II) was developed under ARPA sponsorship. The use of this method in the present study established the relationship of water content to NP stability.

A. STABILITY OF NP VARIES WITH PROTON CONTENT

(C) Initial studies on the relationship of water content to stability were characterized by wide variations in results. Eventually, it became apparent that these variations were due to the complex interaction of water and NP. The study was started with samples from the two bottles of NP mentioned in Section III. The analysis of these samples is given below:

| <u>Source of Samples</u> | <u>Proton Content, Wt. %</u> | <u>Average "wt. % H₂O"</u> |
|--------------------------|-----------------------------------|---------------------------------------|
| Bottle 276-6 | 0.023, 0.017, 0.017, 0.017, 0.025 | 0.18 |
| Bottle 276-138 | 0.033, 0.030 | 0.28 |

1. Gas Evolution Increases with Proton Content

(C) Stability tests on samples taken from these bottles showed a wide variation in gas evolution. However, multiple tests indicated that the stability of the two samples was different. The material from bottle 276-138, which had the higher proton content, gave higher gas evolution. Samples with other proton content were obtained through various treatments.

| <u>NP Source</u> | <u>Number of Samples in Various Thermal Stability Groups</u> | | | | | |
|--|--|-------------------|-------------------|-------------------|-------------------|--------------|
| | <u>Groups based on cc. gas evolved/g. after 100 hrs. at 60°C</u> | | | | | |
| | <u>0 to .20</u> | <u>.21 to .40</u> | <u>.41 to .60</u> | <u>.61 to .80</u> | <u>.81 to 1.0</u> | <u>1.01+</u> |
| 276-6 (0.02 wt. % H ₂) | -- | 2 | 6 | 2 | 2 | -- |
| 276-138 (0.032 wt. % H ₂) | -- | 2 | 3 | 6 | 2 | -- |

Individual proton analysis on these small samples was obtained and then stabilities were determined. These data also indicate that gas evolution increases with proton content. The lack of correlation between proton content and t_c suggests that at this low "H₂O" level other factors are more important.

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Variation of 60°C Stability with Proton Content

| <u>H₂ wt. %</u> | <u>Std. cc./g./100 hrs.</u> | <u>Hours to t_a Acceleration</u> |
|----------------------------|-----------------------------|--|
| 0.022 | 0.52 | 100 |
| 0.023 | 0.56 | >200 |
| 0.033 | 0.74 | 90 |
| 0.040 | 0.72 to 0.92 | 150 to 320 |
| 0.044 | 0.71 | 150 |

The history of each sample was not identical and this appears to have important bearing on the effect of moisture on t_a.

2. Relationship Between Time to Acceleration and 100 Hour Gas Evolution Obscure

(C) The lack of correlation between gas evolution at 100 hours and the time to acceleration indicates that these properties are independent of each other. However, experimental factors may have a great effect as evidenced by the data below.

| <u>NP Source</u> | <u>Number of Samples in Various Acceleration Groups</u> | | | | | | |
|--|---|-----------------|------------------|------------------|------------------|------------------|-------------|
| | <u>Groups based on time to onset of acceleration, Hours</u> | | | | | | |
| | <u>0 - 50</u> | <u>51 - 100</u> | <u>101 - 150</u> | <u>151 - 200</u> | <u>201 - 300</u> | <u>301 - 400</u> | <u>400+</u> |
| 276-6 (0.02 wt. % H ₂) | -- | 10 | 1 | 1 | -- | -- | -- |
| 276-138 (0.032 wt. % H ₂) | -- | 3 | 2 | -- | 2 | -- | 4 |

In contrast to the effect of water content on gas evolution, higher water content gives a better value for t_a. Thus, the sample with the lower water content (276-6) goes auto-catalytic more readily than the higher sample. Also, those samples from bottle 276-138, which gave the largest values of t_a, were the first to be removed from the bottle. Since previous results indicated that fresh Callery NP fluff undergoes "drying" during storage in the dry-box, the scatter from bottle 276-138 may merely represent variation in water content. Even though no general correlation between 100 hour gas evolution and t_a is evident, no samples with extremely low (0.2 cc.) gas evolution at 100 hours have exhibited high values of t_a (300 hours). These observations led us to the conclusion that an increase in water content might also produce higher values of t_a.

B. INTERACTION OF WATER AND NP IS COMPLEX

(C) In the course of the above work on the correlation of water content and stability, proton content determinations were made on various samples of NP. The wide variation experienced in stability tests on samples from bottle 276-138 led us to investigate the homogeneity of the samples with regard to proton content. We attempted to homogenize the NP by grinding it in the dry-box. This and other investigations on the proton content over several months yielded the following data.

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| Sample | H, wt. % |
|---|--------------|
| Top of bottle | 0.058 |
| Top of bottle (Exposed overnight in dry box) | 0.036 |
| Within bottle | 0.037, 0.030 |
| Homogenized #1 (Exposed 19 hours in dry box) | 0.037 |
| Homogenized #2 | 0.020, 0.028 |
| Homogenized #3 | 0.036 |
| Homogenized #3, from VTS prior to heating | 0.018 |
| Homogenized #1, residue from VTS | 0.013 |
| "Moisturized" samples (used moist air flow technique) | |
| 0.5 ppm, 1 hour | 0.025 |
| 4 ppm, 45 minutes | 0.022 |
| 7.5 ppm, 1 hour | 0.027 |
| 15-20 ppm, 20 minutes | 0.044 |

(U) The variation in proton content in these samples is much greater than the experimental error observed in the calibration of the method. At first glance it appears that the NP in bottle 276-138 is very heterogeneous. However, analysis of the other samples shows that the proton content of the samples is subject to change. The magnitude of the change appears limited. Thus, preparing a sample for VTS testing, which includes a 10-minute evacuation, produces a marked decrease in proton content. However, the residue after VTS shows no apparent reduction in proton content. In addition, attempts to increase the proton content by contact with moist air gave mixed results. In some cases the samples became drier than the starting material.

(C) The explanation for these curious results lies in the lability of the H₂O-NP interaction. NP is very hydrophylic and reacts rapidly with water. This reaction can be represented by the following reactions (8).



The expected products from the reaction of water and NP are nitric and perchloric acids (Reaction 1). With a large excess of NP present, these acids would be anhydrous and therefore volatile. However, the adsorption of the acids on the NP cannot be excluded. In fact, there is evidence (8) of a solid, NP-hydrate which has the composition shown in Reaction 2. Finally, the combination of nitric and perchloric acid produces hydronitridium perchlorate (9) shown in Reaction 3. This compound was believed to be a mixture of NP and hydronium perchlorate, H₃OClO₄. However, a more recent interpretation (10) is that it is a mixed crystal system of the two. Furthermore, the NP-hydrate may also represent a similar mixed crystal system with a different composition.

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(C) Whatever its actual composition, hydronitracidium perchlorate exhibits a slight volatility and sublimates as a mixture of nitric and perchloric acids (10). Thus, nitronium perchlorate readily reacts with water, even at very low concentrations; but it also is able to "lose water" by the liberation of nitric and perchloric acids. This explains why NP with a low proton content is subject to change when handled in a dry-box. Under relatively static conditions, water is retained; but under dynamic conditions, "water" is lost.

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VI. WATER TREATMENT OF NP

(C) The proton content study indicated that (1) t_a , the time for the onset of accelerated decomposition, might be increased with water, and (2) the proton content of NP tends to change during handling. Both of these conclusions suggested that water treatment of NP would give better control over NP stability. Further proof of the advantage of added water on t_a was derived from a test in a sample of NP which had inadvertently been exposed to moisture. Convinced of the value of water treatment, we studied the systematic addition of water to NP.

Effect of Moisture on 60°C Stability

| <u>Sample</u> | <u>Std. cc./g./100 hr.</u> | <u>t_a, Hours</u> |
|----------------|----------------------------|--------------------------------|
| Standard 276-6 | 0.41 to 0.60 | 51 to 100 |
| "Wet" 276-6 | 21.0 | >400 |

A. WATER TREATMENT INCREASES t_a GREATLY

(C) Water treatment of NP gives a significant increase in t_a . Treatment of NP with 1.23 wt.% H_2O (10 mole %) gave values of t_a greater than 1000 hours at 60°C. In contrast, untreated NP (0.28 wt.% H_2O) undergoes accelerated decomposition shortly after 100 hours. High values of t_a were consistently found for numerous samples as illustrated in Table I.

1. About 1 Mole % H_2O Lower Limit for Improvement

(C) Further studies (observed in Part B) showed that at around 1 mole % H_2O , this treatment is offset by other factors and t_a remains relatively low. No determination of an upper limit for the effect on t_a was made, since it is desirable to minimize the amount of water added.

TABLE I

60°C Stability of 10 Mole % H_2O - Treated NP

| <u>Sample</u> | <u>Evacuation Temp.</u> | <u>Gas Evolved, Std. cc/g.</u> | | <u>t_a, Hours⁽¹⁾</u> |
|--------------------------|-------------------------|--------------------------------|------------------|--|
| | | <u>100 hours</u> | <u>400 hours</u> | |
| Untreated ⁽²⁾ | 28 to 30°C | 0.72, 0.82 | --- | 100 |
| Batch 1 ⁽³⁾ | -196°C | 0.62 | 1.43 | >690 |
| | 28 to 30°C | 0.50 | 1.43 | >690 |
| Batch 2 | -196°C | 0.46 | 0.98 | >1100 |
| | 28 to 30°C | 0.40 | 0.74 | >1100 |

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TABLE I (Continued)

| Sample | Evacuation Temp. | Gas Evolved, Std. cc/g. | | t _a , Hours ⁽¹⁾ |
|---------|------------------|-------------------------|-----------|---------------------------------------|
| | | 100 Hours | 400 Hours | |
| Batch 3 | -196°C | 0.64 | 1.18 | >550 |
| | 28 to 30°C | 0.50 | 1.02 | >550 |
| Batch 4 | 28 to 30°C | 0.58, 0.42 | | |

- (1) The > symbols indicate no acceleration when run terminated.
- (2) Samples from bottle 276-138 were used in H₂O treatment study. Initial "water" content was 0.28 wt. %.
- (3) Temperature of initial mixing was 28°C; other batches mixed at -80°C.

2. Water Treatment More Complex Than Simple Addition of Water

(C) The water treatment of NP as described here is not just the addition of water to NP, but the entire procedure to prepare the treated sample. The standard treatment (given in detail in Appendix III) consists of the following steps: (1) the vapor addition of water, (2) mixing, (3) overnight storage, and (4) removal of volatiles. The importance of including all these steps is illustrated by the proton analysis results on treated NP. Proton analysis on 10 mole % water-treated NP prior to pumping gave results corresponding to 1.56 wt. % H₂O vs. the expected 1.51 wt. % which was based on the amount of water added and the previous analysis of the NP used. However, an analysis was made on another batch of NP treated with 10 mole % H₂O which had been pumped in a manner similar to that used in VTS preparation. This sample contained only 0.95 wt. % H₂O. Thus the removal of volatiles is an important part of water treatment.

B. WATER TREATMENT AFFECTS GAS EVOLUTION

(C) Our earlier work suggested that the gas evolved from NP at 60°C was related to its water content. Yet, the gas evolution can be decreased by the treatment of NP with 10 mole % water. This point is substantiated by the data summarized in Table I. The data also show that evacuation of the test sample at -196°C (to minimize loss of volatiles) gives a small but consistently higher gas evolution. These results probably reflect (1) an actual difference in test samples, and (2) a major loss of volatiles during the loading of samples into the test units in the dry-box.

1. 5 to 15 Mole % H₂O Treatment Gives Minimum Gas Evolution

(C) Since a marked increase in t_a was observed over a wide range of water treatment levels, emphasis was next placed on the relationship of gas evolution to the water treatment level. Water treatment was carried out at water levels of 0.5, 1, 5, 10, and 20 mole %. The 60°C stability tests showed that at the 5 to 15 mole % treatment levels, gas evolution is a minimum. This is illustrated in Figure 4.

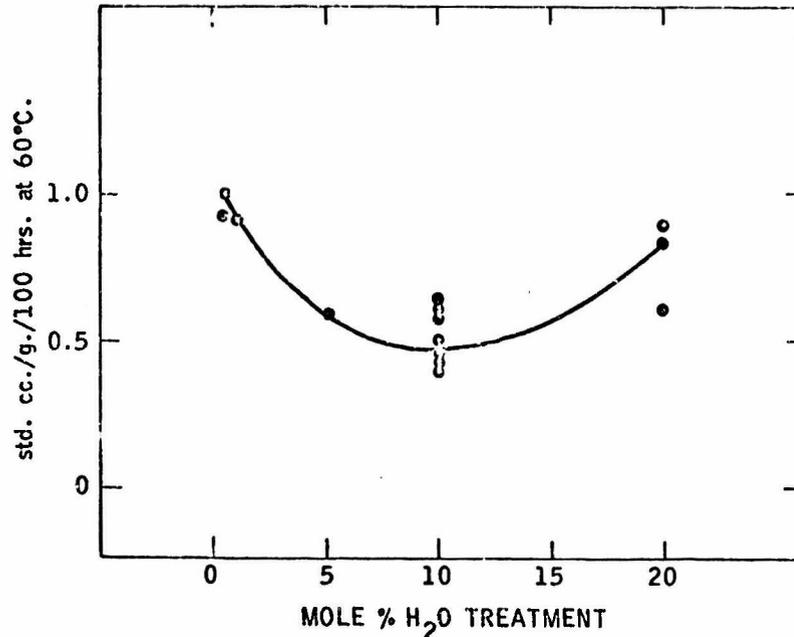
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Figure 4

Effect of H₂O Treatment Level on NP Stability (C)



Although lower values of gas evolution after 100 hours at 60°C can be achieved by vacuum drying of NP, the desired combination of high values of t_a and low values of gas evolution made water treatment more attractive for the stabilization of NP. The above data indicated that a minimum quantity of stabilizer was necessary. Previous experience indicated that treatment conditions were important. Therefore, we initiated a study to optimize the treatment.

2. Treatment Procedures Important

(C) Our earlier studies on the relationship of water to NP stability showed that dynamic factors could be of major importance. Therefore, we suspected that treatment procedures would influence the treatment. Our suspicions were confirmed by subsequent investigations.

a. Mixing Important

(C) Early in the water treatment study a 48 mole % water treatment was made. At the end of this treatment, the volatile gases were condensed into another bulb. On warming to room temperature, the bulb contained both a liquid and red-brown fumes. This suggested that nitric acid was formed. Nitric acid is deleterious to the stability of NP and its formation in sufficient quantity may cause the higher gas evolution noticed at the higher treatment levels. Similar results would be expected to arise from localized high water concentration during treatment. To avoid this problem in our water treatment, water was added slowly in the vapor state with constant agitation.

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b. By-Product Removed During Treatment

(C) During the water treatment study a series of pressure measurements were made prior to sampling the treated material. These measurements show that the pressure above the treated NP was approximately 7 mm. The pressure was independent of treatment level (1 to 10 mole %) and contact time (3 to 40 days). This suggests that the vapor is in equilibrium with the solid. After a 10-minute evacuation and 8 days of standing, the pressure over a treated sample was only a few tenths of a millimeter of Hg. A repeat of this treatment gave no further reduction in pressure. Thus, during the treatment a highly volatile by-product is removed and a low volatile stabilizer remains on the treated material.

(C) Mass Spectral analysis of the by-product vapor indicated a mixture of water and nitrogen oxides. However, we interpret this as nitric acid which is removed during subsequent handling in the dry-box and evacuation prior to stability testing. The absence of O_2 and CO_2 in this vapor suggests that no decomposition occurred during water treatment.

c. Prolonged Pumping Detrimental

(C) Short intermittent pumping of 10 mole % H_2O -treated NP did not produce any significant change in $60^\circ C$ stability. Thus, a sample subjected to three 10-minute pumping periods during eighteen days of storage at room temperature gave the following stability data.

| Sample | <u>60° Stability</u> | | |
|------------------------------------|--|----------------------|-------|
| | Std. cc/g./100 Hours | Std. cc/g./400 Hours | t_a |
| Standard 10 mole % H_2O -treated | 0.40 to 0.58 | 0.74 to 1.43 | >1100 |
| Same, after intermittent pumping | 0.40, 0.44 | 0.92, 1.01 | >950 |

(C) In contrast to this behavior, samples of 10 mole % water-treated NP subjected to six hours of extended pumping have shown very poor stability.

| Sample* | <u>60° Stability</u> | |
|---------------------------------|--|-------|
| | Std. cc/g./100 Hours | t_a |
| No. 1 after 6 hours pumping | 1.9, 2.0 | 60 |
| No. 2 after 6 hours pumping | 1.18 | 80 |
| No. 3 after 5-1/2 hours pumping | 0.46 | 110 |

* All samples from various batches of 10 mole % water-treatment.

(C) Based on proton analysis, a pumped sample still contained a large amount of water (1.4 wt.% vs. 1.5 wt.% for the unpumped samples). This loss of protection against the onset of accelerated decomposition (t_a) with only a small loss in water content emphasizes the complexity of the stabilization. Thus, to be effective, the stabilizer must be maintained on the active surface sites.

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d. Pumping Effect Temperature Dependent

(C) From the results of various experiments on the effect of treatment variables we concluded that the stabilization effect of water treatment arises from a low volatility stabilizer that can be removed by extended pumping. To test this conclusion, pumping experiments were made at lower temperatures. The results showed that below 0°C pumping for six-hour periods is not detrimental to t_a . Thus, reduced temperature pumping should give better separation of the more volatile by-product(s) without loss of the stabilizer.

60°C Stability

| <u>Pumping Temp.*</u> | <u>Std. cc/g./100 hours</u> | <u>Std. cc/g./400 hours</u> | <u>t_a, hours</u> |
|----------------------------|-----------------------------|-----------------------------|--------------------------------|
| (10 minutes at 27 to 30°C) | 0.42, 0.62 | 1.28, 1.66 | > 1100 |
| 27 to 30°C | 1.18 | ---- | 80 |
| 0°C | 0.64 | 1.86 | > 1100 |
| -8 to -12°C | 0.68 | 1.52 | > 1050 |

* Pumping period was six hours.

e. Contact Time and Aging Have Limited Effect

(C) The standard water treatment procedure involves overnight storage. This storage is started at -80°C and usually ends at room temperature. Omission of this step and minimization of the time between H₂O treatment and testing produced excessive gassing during evacuation prior to VTS testing at 60°C. In some cases the -80°C overnight storage was omitted and the treated sample was stored at room temperature for three days. This process was equivalent to the -80°C treatment. In view of these observations, we investigated longer contact times. Specifically, we hoped that prolonged contact might improve the lower level treatments. However, the data failed to support this view.

Effect of Contact Time in Water Treatment

| <u>Water-Treatment Level</u> | <u>Contact Time, Days</u> | <u>50°C Stability</u> | | |
|------------------------------|---------------------------|-----------------------------|-----------------------------|--------------------------------|
| | | <u>Std. cc/g./100 hours</u> | <u>Std. cc/g./400 hours</u> | <u>t_a, hours</u> |
| 10 mole % | 3 | 0.40 to 0.58 | 1.12, 1.58 | > 1100 |
| 10 mole % | 39 | 0.71, 0.34 | 1.28, 0.86 | > 600* |
| 10 mole % | 33 | 0.42, 0.62 | 1.28, 1.66 | > 1100 |
| 5.0 mole % | 38 | 0.40, 0.52 | 1.08, 0.92 | > 400* |
| 3.2 mole % | 40 | 0.72, 0.64 | 1.30, 1.32 | 700, > 400* |
| 1 mole % | 34 | 0.54, 0.60 | 2.10, 1.98 | 400 |
| 1 mole % | 33 | 0.48, 0.54 | 3.90, 3.68 | 100** |
| 1 mole % | 25 | 0.96, 1.02 | 2.90, 3.54 | 60, 100 |
| 1 mole % | 33 | 1.86, 1.32 | 4.26, 3.86 | 1*** |

* Plugging of manometer prevented determination of t_a .

** Not a true acceleration; rate suddenly increased by a factor of 2.5, then remained constant.

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Effect of Contact Time in Water Treatment (continued)

| <u>Water-Treatment Level</u> | <u>Contact Time, Days</u> | <u>60°C Stability</u> | | |
|------------------------------|---------------------------|-----------------------------|-----------------------------|-----------------------------|
| | | <u>Std. cc/g./100 hours</u> | <u>Std. cc/g./400 hours</u> | <u>t_g, hours</u> |
| 1 mole % | 5 | 1.25, 1.44 | --- | 60 |
| 1 mole % | 3 | 0.92, 1.00 | 2.0, 2.2 | 7*** |
| 0.5 mole % | 30 | 0.88, 1.02 | 3.20, 2.16 | 100, 150 |
| 0.5 mole % | 35 | 1.18, 1.26 | 3.22, ---- | 100, 100 |

*** Acceleration not discernible.

(C) The early results in the above study indicated that increased contact time was beneficial both to gas evolution and t_g; but, later results failed to confirm this. We therefore concluded that approximately 1 mole % water treatment represents a critical level at which stabilization can be obtained. However, this stabilization can readily be "reversed" by minor changes in experimental technique. Hence, wide variations are experienced and treatment at this low level is not reliable.

f. Effect of Sample Size Uncertain

(C) The evaluation of treatment conditions was carried out with 2.5 gram samples of NP. In other studies, as the need for treated NP became greater, larger treatments were carried out. The size was first increased to 10 grams and finally to 30 grams with several different bottles of NP. Over this size range, 10 mole % water treatment was carried out successfully. Large-scale treatment may present problems not encountered in the laboratory work. Localized high concentrations of water would be expected to induce decomposition. Thus, large-scale treatment could involve mixing problems.

g. Water Treatment May Vary with NP Samples

(C) Several different samples of NP were used in the water treatment study. The samples were all Gallery prepared fluff but some were from different lots with different histories. The effect of water treatment of these samples showed some variation. Treatment of an older sample previously used in ARPA propellant work did not show any improvement. The lack of improvement arises from the good stability exhibited by the untreated sample.

| <u>Sample</u> | <u>60°C Stability</u> | | |
|---|-----------------------------|-----------------------------|-----------------------------|
| | <u>Std. cc/g./100 hours</u> | <u>Std. cc/g./400 hours</u> | <u>t_g, hours</u> |
| Old Sample | 0.48, 0.50 | 0.96, 1.08 | > 800, >1000 |
| Old Sample after 10 mole % water-treatment | 0.54, 0.62 | 1.10, 1.26 | >800, >500 |

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The explanation of this probably lies in the history of the sample. It was originally opened in a dry-box which was less efficient than those used in the present stability work. The sample had been resealed and stored under atmospheric conditions. It is very likely that previous handling resulted in an unintentional water treatment. Thus, further water treatment was without benefit.

(C) During our studies the NP in bottle 276-138 was exhausted. Another bottle, designated 323-125, from the same lot was opened. Since the previous bottle had been stored in the dry-box prior to water treatment, we anticipated that this freshly opened material would contain more water. Therefore, the sample was pumped prior to water treatment. The data below show that the two different samples gave similar results.

| Sample | 60° Stability | |
|---|------------------------|------------------------|
| | Std. cc./g./100 hrs. | t _a , hrs.* |
| 276-138-Untreated | 0.72, 0.82 | 100 |
| 276-138-10 mole % H ₂ O-Treated | 0.40 to 0.58 | >1000 |
| 323-125-Untreated | 0.26, 0.26, 0.30, 0.60 | 100, 100, 110, 90 |
| 323-125-Pumped 16 hrs. | 0.36, 0.44 | 110, 100 |
| 323-125-Pumped 16 hrs. then 10 mole % H ₂ O-Treated | 0.38, 0.32, 0.58 | >1040, >1040, >500 |

* Values with > signs indicate test was terminated without any indication of acceleration.

(C) Based on these results, we have concluded that water treatment of NP is reproducible providing similar samples are used. NP samples with widely different histories should be tested to determine if water treatment is necessary.

C. STABILITY TEST INVESTIGATED

1. Replicate Tests Show Accuracy

(C) To provide a basis for comparing gas evolution values of different samples, we ran replicate tests (6 each) on two different samples of water-treated fluff. In each case, the average value and the standard deviation(s) was calculated. The following table shows the range, average value and 95% confidence level for these samples.

| Sample | Gas Evolution at 60°C | |
|--|-----------------------|--------------------|
| | Range | Average Value ± 2s |
| 10 mole % H ₂ O Treated NP | 0.22 to 0.46 | 0.32 ± 0.18 |
| 10 mole % H ₂ O Treated NP after prolonged -80°C Storage | 0.88 to 1.08 | 0.97 ± 0.14 |

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These samples represent two extremes in the various samples at 10 mole % water-treated NP tested in this study. The values of the 95% confidence levels show that the accuracy is fair. The variation between the samples further illustrates the variation of water treatment with treatment conditions.

2. Mercury-Free Results Similar to Standard Test

(C) The possibility that mercury from the manometer might influence the VTS results led us to stability tests in mercury-free units. These units (Appendix I) utilized a glass membrane as a null device. Because of the nature of the measurements and the limited availability of the all glass units, only a few tests were made. The results of these tests show only minor variation and do not alter the conclusions based on the tests in the manometer units.

| Run No. | Sample* | 60°C Stability in all Glass Units | | | | | |
|---------|------------------|-----------------------------------|------------|------------------|-----------------------|----------------------|-------------------------|
| | | Unit Volumes, cc. | Volume Wt. | Initial Pressure | Std. cc./g./ 100 hrs. | Std. cc./g. 400 hrs. | t _a , hrs.** |
| 1 | 0.5 g. pellets | 19.9 | 39.8 | 5.6 mm | 0.97 | 2.52 | >1200 |
| 2 | 1.0 g. fluff | 14.8 | 14.8 | 5.8 | 0.50 | 1.64 | >1100 |
| 3 | 1.16 g. fluff | 20.8 | 17.9 | 7.0 | 0.72 | 1.84 | >800 |
| 4 | 1.16 g. fluff*** | 20.8 | 17.9 | 8.8 | 0.50 | 2.59 | >500 |

* All samples are 10 mole % water-treated.

** Runs terminated after runs became erratic (see text).

*** Run made in presence of 803 mm of air.

(C) The general results in the glass units parallel those obtained in the Hg-manometer units. In the latter, some reaction occurs between the gaseous products and the mercury in the manometers. However, the net result of this interaction is a small reduction in the measured gas evolution. In runs 1 through 3 the gas evolution increases with increasing unit volume/sample weight ratio. This relationship is not linear and it gives greater variation at lower ratio values. Some deviation in the results may arise from the use of different batches of 10 mole % water-treated NP in the first three runs. Run 4 utilized NP from the same batch as run 3 and was also run in the presence of 803 mm of dry air. The effect of air is not clear at this time. The rate of gas evolution increased after 100 hrs.; but, the decomposition was not autocatalytic when the run was terminated. All runs were terminated after the build-up of sublimate (presumably the stabilizer) on the glass diaphragm which caused erratic operation.

(C) The initial pressures should correspond to the vapor pressure of the volatile stabilizer. The variation in these pressures between runs 1 and 2 and runs 3 and 4 are greater than experimental error. This suggests that the volatility of the stabilizer may vary among different batches of water-treated NP.

(C) A run was also attempted at 40°C. After 165 hrs., the gas evolution was approximately 0.05 std. cc./g. This low gas evolution suggests that at lower temperatures water-treated NP exhibits very good stability. Thus, long term storage should be feasible. In addition, the initial pressure was below 1 mm which gives an upper limit for the volatility of the stabilizer at this temperature.

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D. NATURE OF THE STABILIZER

(C) Early work on water treatment suggested that NP stabilization by water depends on the formation of a particular hydrolysis product rather than a particular water content. We first noticed this when H₂O-treated NP samples were mixed with untreated NP in the ratio of 1/4. From 0.5, 1.0, 5, 10 and 20 mole % H₂O-treated NP, mixtures were made that contained 0.1, 0.2, 1.0, 2.0 and 4.0 added water. The stability results from these mixtures are shown in Table II. The hydrogen analysis of the untreated NP corresponds to 2.2 mole % H₂O. Therefore, no significant change was expected for the two lower mixtures. Surprisingly, the stability of the mixture with 2 mole % added water was similar to that of the 10 mole % water-treated sample from which it was made. This indicates that a mobile stabilizer is formed.

TABLE II

60°C Stability of NP Mixtures
Mixture: 1/4 H₂O-treated NP/Untreated NP

| <u>H₂O Treated Sample</u> | <u>Std. cc./g.</u> | | <u>t_a, hrs.</u> | <u>Evacuation Temp., °C</u> |
|--|--------------------|-----------------|----------------------------|-----------------------------|
| | <u>100 hrs.</u> | <u>400 hrs.</u> | | |
| Untreated (2.2 Mole % H ₂ O)* | 0.72, 0.82 | ---- | 100 | 28 to 30 |
| 0.5 Mole % H ₂ O-Treated | ---- | ---- | 70 | 28 to 30 |
| 1 Mole % H ₂ O-Treated | 1.12 | ---- | 100 | 28 to 30 |
| 5 Mole % H ₂ O-Treated | 0.76 | ---- | 160 | 28 to 30 |
| 10 Mole % H ₂ O-Treated | | | | |
| Batch 1 | 0.52 0.48 | 1.76 1.26 | 550** 550* | -196 28 to 30 |
| Batch 2 | 0.58 0.38 | 1.86 1.12 | >690 950 | -196 28 to 30 |
| Batch 3 | 0.68 0.58 | 1.72 1.58 | >550 >550 | -196 28 to 30 |
| 20 Mole % H ₂ O-Treated | 0.74 | ---- | >360 | -196 |

* Based on hydrogen analysis.

** Acceleration slow.

1. Hydronitricidum Perchlorate Believed to be the Stabilizer

(C) The probable presence of nitric acid above water-treated NP suggested that the products of the water-treatment process are nitric acid and hydronitricidum perchlorate, H₃NO₃(ClO₄)₂. Thus, the overall reaction of the water treatment may be represented by the following:



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Additional evidence was found for this reaction. A sample of 10 mole % water-treated NP was pumped for 6 hours. During this time a small amount of white solid was collected in a trap at -196°C . The analysis of this solid agrees with that expected for $\text{H}_3\text{NO}_3(\text{ClO}_4)_2$.

| <u>Analysis</u> | <u>Found</u> | <u>Calculated for $\text{H}_3\text{NO}_3(\text{ClO}_4)_2$</u> |
|-----------------|--------------|--|
| % N | 5.36 | 5.31 |
| % Cl | 25.0 | 26.9 |

The removal of this solid from the treated NP sample resulted in loss of stability giving t_a values below 100 hrs. This indicates that hydronitracidium perchlorate is responsible for the stabilization imparted by water treatment.

(C) In another experiment, 10 mole % water-treated NP was pumped on for a much longer period at room temperature. We found that the sublimation was a very slow process. The accumulated sublimate was collected at -196°C . With it was a small amount of liquid which was removed by short pumping at room temperature. The analysis of the recovered sublimate was in good agreement with expected values for hydronitracidium perchlorate.

| <u>Analysis</u> | <u>Found</u> | <u>Calculated for $\text{H}_3\text{NO}_3(\text{ClO}_4)_2$</u> |
|-----------------|--------------|--|
| Wt. % N | 4.95 | 5.31 |
| Wt. % Cl | 26.58 | 26.87 |

To demonstrate the effectiveness of this solid, a mixture with untreated NP was prepared. The mixture of 4.56 mole % $\text{H}_3\text{NO}_3(\text{ClO}_4)_2$ in untreated NP gave the following results.

| <u>Sample</u> | <u>60°C Stability</u> | |
|--|-----------------------------|-------------------------|
| | <u>Std. cc./g./100 hrs.</u> | <u>t_a</u> |
| Untreated NP (323-125) | 0.26 to 0.60 | 90 to 110 |
| 4.56 mole % $\text{H}_3\text{NO}_3(\text{ClO}_4)_2$ in untreated NP (323-125) | 0.50 | > 600 |

(C) We also attempted to measure the stability of a neat sample of hydronitracidium perchlorate. The initial gas evolution was high but constant at 1.04 std. cc./g. from 20 to 90 hours. At hour 90, the quantity of gas evolved increased, but thereafter the rate decreased. At 300 hrs. the total gas evolution was 2.26 std. cc./g. We do not know if these data reflect the presence of small amounts of impurities or the true nature of hydronitracidium perchlorate.

2. Characteristics of Stabilizer Important

(C) To understand the various results concerning the water-stabilization of NP, a knowledge of the characteristics of the stabilizer is required. The known characteristic of hydronitracidium perchlorate provides a basis for many of the observed, apparently contradictory, results on NP stability.

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a. Stabilizer Slightly Volatile

(C) The volatility of the stabilizer has been demonstrated by various observations including its sublimation. The data on water-treated NP indicates a vapor pressure around 6 to 9 mm at 60°C, less than 1 mm at 40°C and very low below 0°C. Volatility measurements also indicate that at -30°C the vapor pressure is quite low, probably below 1 micron. This slight volatility explains why the water treatment of NP can be "reversed". Pumping removes part of the stabilizer and thus leads to lower stability. Similarly, the variation of stability with the ratio of sample weight/test volume is explained. Other implications of this volatility are discussed below.

b. Vapor Equilibrium Slow

(C) Although the stabilizer is volatile, the isolation experiments showed that sublimation is a slow process. To some extent the results appeared contradictory since a small amount is readily transferred in the vapor; but, larger amounts move very slowly. However, studies on hydronitracidium perchlorate (10) have shown that the vapor transfer occurs as a mixture of nitric and perchloric acids. Thus, the sublimation involves a dissociation as well as vaporization. Since the vapor pressure is well below that of the individual anhydrous acids, the dissociation is the controlling factor. From the slowness of continuous sublimation, it appears that the dissociation, particularly in the presence of excess NP, is a slow step and it is rate determining for sublimation. This phenomenon, in part, gives rise to the wide variation in results among similar stability tests.

c. Composition Variable

(C) Ingold (11) postulated that hydronitracidium perchlorate was composed of an equimolar mixture of NP and hydronium perchlorate of H_3OClO_4 . However, more recent work at Callery Chemical Co. has shown that the physical properties are not those of such a mixture. Instead, they reported that nitracidium perchlorate is best described as a "mixed crystal system" of nitronium perchlorate and hydronium perchlorate. This designation infers that over certain limits, as yet undetermined, an intimate mixture of these two materials forms a new phase with different properties. Thus, "hydronitracidium perchlorate" is not a compound with an exact composition, but it is a solid phase which exists over a range of composition and exhibits unique properties.

3. Mechanism of Stabilization Implied

(C) Based on kinetic studies (1), the decomposition of NP arises from active sites on the surface of NP particles. From the observations on water-stabilized NP and the properties of the stabilizer, we suggest the following mechanism for the stabilization of NP by water treatment. The reaction of water with NP leads to the formation of hydronium perchlorate. The incorporation of this material in the crystal structure of NP leads to the formation of a new phase on the surface of the NP crystal. Either the formation process or the presence of this new phase causes deactivation of the reaction sites. This may be effected by removal of crystal faults, relaxation of crystal strain or by the modification of the surface environment. According to this mechanism, the prime consideration for the selection of other stabilizing agents is not potential scavenging effects but instead the crystal structure of the additive.

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(C) This mechanism implies that a stabilizer must be in intimate contact with the surface of the NP and that a sufficient quantity must be present to deactivate most of the active sites. These considerations led to the following requirements necessary for an additive to be effective as a stabilizer for NP: (1) the crystal structure must be very similar to the structure of hydronium perchlorate, (2) the additive must be well distributed over the surface of the NP (this implies an in situ formation, a volatile additive or the use of a compatible solvent), and (3) preferably, the additive should have a low volatility.

4. Problems in Utilization

(U) Because of the nature of the stabilizer, there are some problems in its utilization. The two main problems arise from its volatility. These problems concern the stability of the stabilizer and the coatibility of the treated NP.

a. NP Requires Coating

(U) The volatility of the stabilizer also imparts mobility to it. Although this mobility aids in the distribution of the stabilizer to the active sites which it must deactivate, it also facilitates the removal of the stabilizer. This removal necessitates the use of excess stabilizer to control minor losses. More important, it means that the NP must be coated to prevent significant losses of the stabilizer and maintain continuous stabilization. Unless some other stabilizer is found that imparts water resistance to NP, it is unlikely that unprotected NP can exhibit any long-range stability.

b. Volatility Complicates Coating Operation

(C) The most attractive coating for NP, at the present time, is the "Rete" coating developed by Union Carbide (12). This coating appears good in both protection and compatibility. However, it is formed in situ in a vacuum process. The vapor pressure of 10 mole % water-treated NP is sufficient to interfere with the operation. Therefore, unless some means of controlling the volatility is found, this coating cannot be applied to water-treated NP.

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VII. MODIFICATION OF WATER-TREATED NP

(C) Since the volatility of water-treated NP interfered with the application of a "Reta" coating, we investigated methods for modifying the treated NP. These methods involve two approaches, precoating of the treated NP and chemical modification.

A. PRECOATING PARTIALLY SUCCESSFUL

(C) Initial attempts to improve the coatability of water-treated NP involved devolatilization. Earlier work showed that a volatile by-product, presumably nitric acid, is formed during water treatment. It appeared that removal of this volatile material was incomplete. Data from a 10 gram batch of 10 mole % water-treated NP illustrate this slow removal of volatiles. Unfortunately, extended pumping results in loss of stability due to the volatility of the stabilizer. Therefore, an investigation of precoating NP for volatility reduction was undertaken.

| <u>Pumping Time</u> | <u>Equilibration Time</u> | <u>Pressure</u> |
|---------------------|---------------------------|-----------------|
| 0 | 5 days | 10 mm |
| 5 min. | 1.5 hours | 3 mm |
| 10 min. | 2 hours | 2 mm |

1. Procedures Modified

(U) The investigation of volatility reduction required new procedures and materials. These involved low pressure measurements, the use of pellets of NP and various Kel-F waxes.

a. Volatility Measurements

(U) Measurements were made to determine the volatility reduction of various treatments. These measurements were made with a Hastings thermocouple gauge (Model VT-5B). This gauge was calibrated for air. Because of the nature of the volatile materials involved, we made no attempt to calibrate the gauge for these gases. Thus, absolute pressures were not obtained. The relative measurements, however, were sufficient to measure significant decreases in volatility. In conjunction with the volatility measurements, we also obtained stability measurements to augment our findings.

b. Pellets Use In Precoating Study

(C) Pellets are much more attractive for coating than the fluff. Therefore, in our precoating study we water-treated NP fluff, pelletized the product and then coated the pellets. Pellets with a 1/3 inch diameter were made in a Parr hand press. The stability of the pellets is about the same as that obtained with the fluff.

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| Sample* | 60°C Stability | | t _a ** |
|------------------|----------------------|----------------------|-------------------|
| | Std. cc./g./100 hrs. | Std. cc./g./400 hrs. | |
| Fluff | 0.40 to 0.58 | 0.74 to 1.43 | >1100 |
| 1/8 inch pellets | .46, .42 | 1.04, 1.10 | >570 |
| 1/8 inch pellets | .46, .36 | .80, .78 | >550 |
| 1/8 inch pellets | .38, .46 | 1.06, 1.1 | >650 |

* All 10 mole % water-treated.

** Test terminated without evidence of accelerated decomposition.

c. Kel-F Waxes Used For Precoat

(U) The two main requirements for a precoating for NP are (1) the material must be compatible with NP and (2) the application must not utilize elevated temperatures or incompatible solvents. In view of these requirements, our choice of a precoating material was a halofluorocarbon polymer. In initial tests we found the Kel-F waxes were compatible with NP and these materials were used in most of our precoating studies.

2. Results of Precoating with Kel-F

a. Solvents Give Rise to Volatility

(U) The application of Kel-F to NP pellets was carried out by dissolving the wax in a Freon solvent, swirling the pellets in the solution, pouring off the solution, and drying the pellets. In an initial attempt, pellets were immersed in Kel-F 40 and then rinsed with Freon 113 to remove excess wax. Stability testing of these pellets indicated that incomplete solvent removal was a problem. This was also indicated by precoating with Kel-F 200 wax.

| <u>Sample</u> | <u>Std. cc./g./100 hrs. at 60°C</u> |
|---|-------------------------------------|
| Uncoated 1/8 inch pellets | 0.38, 0.46 |
| Kel-F 40 coated pellets | 0.70 |
| Kel-F 40 coated pellets after 4-1/2 hours of pumping | 0.46 |

Pellets coated with Kel-F 200 deposited from Freon 11 gave relatively poor volatility. Freon 11 was chosen as a solvent rather than Freon 113 because of its lower boiling point. Thus it should have been removed more easily. However, Freon 11 shows greater solubility for the wax, so we made volatility measurements on the wax deposited from each solvent in the absence of NP. The results indicated that the Freon 113 is more readily removed. Therefore, Freon 113 was used in subsequent experiments.

(U) A later test was also made on precoated, untreated NP. In this experiment untreated NP was pumped on to remove traces of hydronitracidium perchlorate. After pre-coating with a 50/50 mixture of Kel-F 40 and Kel-F 200, the volatility at -40°C was extremely high. This result also indicates that part of the volatility is due to incomplete solvent removal.

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b. Kel-F Precoating Decreases Volatility

(C) In order to minimize the contribution from the solvent, we pumped the pre-coated pellets for extended periods prior to the volatility measurements. After the pumping period, pressure measurements were noted at various intervals of time. The data below show a decrease in volatility for the pre-coated water-treated pellets.

Volatility Measurements

| <u>Sample</u> | <u>Time of Reading Min.</u> | <u>Arbitrary Gauge Reading</u> |
|---|-----------------------------|--------------------------------|
| Thiokol pellets-pumped 23 hrs. | 33 63 | 49 85 |
| 10 mole % water-treated Pelletized, pumped 26 hrs. | 32 61 | 53 85 |
| Kel-F 200 coated/Freon 113 Pelletized, pumped 43 hrs. | 41 55 | 35 54 |
| Pelletized, Kel-F 40/200 coated/ Freon 113, pumped 40 hrs. | 32 67 | 26 46 |

(C) After the volatility measurements, the same pellets were subjected to stability tests. The combined volatility and stability data show that pre-coating with Kel-F reduces the volatility and increases the retention of the stabilizer under pumping conditions. Nevertheless, some of the stabilizer was lost and stability was decreased as indicated by the value of t_a . Also, pre-coating before pelletizing apparently gives high values of t_a but also increases the solvent removal problem.

| <u>Sample*</u> | <u>60°C Stability</u> | | |
|--------------------------|-----------------------------|-----------------------------|-------------------------------|
| | <u>Std. cc./g./100 hrs.</u> | <u>Std. cc./g./400 hrs.</u> | <u>t_a, hrs.</u> |
| Kel-F 200 pre-coated | 1.20 | 1.78 | 750 |
| Kel-F 40/200 pre-coated | 0.74 | 1.39 | 450 |
| Pelletized, unpre-coated | 0.46 | 2.15 | 200 |

* Greater details of sample given in table above.

An attempt was also made to strengthen the 50/50 mixture of Kel-F 40 and Kel-F -200 by rolling the pre-coated pellet in magnesium oxide which had been passed through a 200 mesh screen. The volatility of the sample was measured at -40°C and found to be extremely high. After warming to room temperature, pumping and re-cooling, the volatility was reduced at -40°C. However, at room temperature, the sample had considerable volatility and this approach was abandoned.

c. Low Temperature Precoating Unsuccessful

(C) We realized that the volatility of water-treated NP would make it difficult to achieve an unbroken precoat. Also, volatility measurements on the 10 mole % water-treated NP pellets showed that between -30 and -40°C the volatility is very low. In addition, 10 mole % water-treated NP pumped 6 hrs. at low temperatures showed no loss in stability.

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Therefore, we attempted solvent removal by pumping at -30°C for several days. Volatility measurement at -40°C indicated that the solvent had been removed. However, measurements at -20°C showed volatility. Thus it appears that the thin precoating of Kel-F 40/200 is not strong enough to retain the volatile stabilizer completely. Furthermore, recent work (13) has shown that during the "Reta" coating process some heating occurs on the surface of the pellets. Thus, precoating with Kel-F waxes is not effective enough to permit "Reta" coating of water-treated NP.

B. DUAL TREATMENT GIVES MIXED RESULTS

(C) Since difficulties were encountered in our precoating studies on water-treated NP, we looked for some other method of volatility reduction of water-treated NP. Therefore, we investigated chemical treatment as a means of modifying the stabilizer.

1. Approach Based on Stabilizer

(C) Removal of the stabilizer results in loss of stability; thus, no drastic change in the structure of the stabilizer is desired. Although the crystal structure of NP is monoclinic (14), that of hydronium perchlorate is orthorhombic (15). The structure of the mixed crystal system is not known; but, if hydronium perchlorate in it was replaced by another orthorhombic crystal of the same size, no change in structure would be expected. The X-ray patterns of ammonium perchlorate and hydronium perchlorate are identical (15); therefore, the structures are identical. Hence, we anticipated that reaction of water-treated NP with ammonium should produce a mixed crystal system of NP and ammonium perchlorate on the surface of the NP. In addition to the reduction in volatility, this mixed crystal system might have other benefits. Ammonium perchlorate is not hydrophilic; therefore, it might protect NP from moisture to some extent. However, it is unlikely that treatment of NP with ammonium perchlorate would be effective, since this treatment would lack the intimate contact necessary for the formation of a mixed crystal system.

2. Ammonia Treatment Partially Effective

(C) Our initial attempt on the dual treatment of NP involved a 10 mole % ammonia treatment of a sample of 10 % water-treated NP. After this treatment, the stability results looked promising. The initial volatility measurements were apparently affected by the residual ammonia.

| Sample | 60°C Stability | | |
|---|----------------------|----------------------|---------------|
| | Std. cc./g./100 hrs. | Std. cc./g./400 hrs. | t_{90} hrs. |
| NH ₃ treated, H ₂ O-treated NP | 0.28 | 1.01 | >1000 |
| Pellets of H ₂ O-treated NP/ treated with NH ₃ | 0.52 | 1.12 | >1000 |

(C) In most of the continuing work on this dual treatment, the NP fluff was pumped 6 hours after the NH₃ treatment. The purpose of this was two-fold: (1) residual ammonia is removed and (2) the stability results after this pumping served as a check on the volatility reduction.

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a. Treatment Conditions Affect Treatment

(C) A number of treatments were made under varying conditions. The results summarized in Table II show wide variations with different treating conditions. It should be noted that most of the stability results were obtained after the samples had been pumped for 6 hours at room temperature. This pumping procedure was employed to demonstrate the reduction in volatility of the stabilizer.

TABLE II

Ammonia Treatment of 10 Mole % Water-Treated NP(C)

| Treatment Level | Conditions | Pumping Period,* hrs. | 60°C Stability | | t _a ** hrs. |
|--|---|-----------------------|-----------------------|-----------------------|------------------------|
| | | | Std. cc./g./ 100 hrs. | Std. cc./g./ 400 hrs. | |
| 5 mole % | 27°C, large reactor Above material pelletized | 6 | 4 | -- | < 60 |
| | | 20 | 1.06 | 1.90 | >800 |
| 5 mole % | 27°C, NH ₃ condensed in | 6 | 1.20 | 2.57 | 810 |
| 5 mole % | -30°C, large reactor Above material pelletized | 1 | 0.46 | 1.20 | >670 |
| | | 21.5 | 0.50 | 1.30 | >600 |
| 10 mole % | 27°C, small reactor 27°C, small reactor | 6 | 0.57 | 2.46 | 560 |
| | | 6 | 0.48 | 0.92 | >900 |
| 10 mole % | -30°C, large reactor Above material pelletized | 6 | 1.16 | -- | 80 |
| | | 6 | 0.62 | 1.48 | >480 |
| | | 24 | 0.66 | 1.76 | 340 |
| 15 mole % | -30°C, large reactor Above material pelletized | 6 | 1.28 | -- | 150 |
| | | 6 | 0.66 | 1.48 | 450 |
| | | 52 | 0.58 | -- | 230 |
| (10 mole % H ₂ O-treated starting material) | | 0.1 | 0.32 | 0.68 | (700) |
| | | 5.5 | 0.46 | -- | 110 |

* Total cumulative hours for pellets.

** Greater than signs indicate runs terminated without accelerated decompositions.

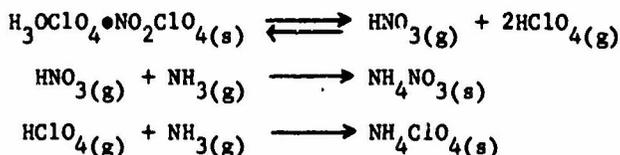
Previous experience with water-treated NP has shown that pumping can offset the stabilization effect of water treatment. Thus, most of the data shows that some volatility reduction was achieved.

(C) The variation with treating conditions was not surprising in view of the observations made during the treatments. In the runs at room temperature, a white solid was formed on the upper walls of the reactor. Obviously, dissociation of the stabilizer causes reactions in the gas phase. Thus, in the larger reactor where the gas phase reactions are favored, we observe some loss in stability.

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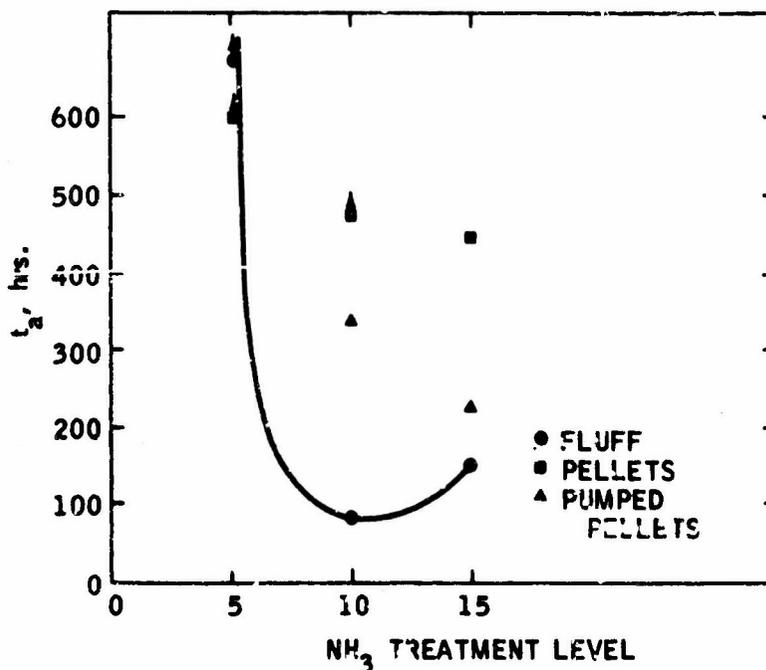
Condensing the NH_3 onto the NP and then warming to room temperature apparently favors the surface reaction and gives rise to higher values of t_a . However, the large concentrations of NH_3 may also promote reaction with the NP rather than the stabilizer, thus giving higher gas evolution. To facilitate the surface reaction, we added gaseous ammonia to the water-treated NP at low temperatures, ca. -30°C . This gave results that are difficult to explain.

b. Fluff and Pellets Gave Different Results

(C) The effect of the treatment at -30°C is not clear. Furthermore, the effect of pelletizing this material is most surprising. In those cases for which the treated fluff gives low values of t_a , pelletizing appears to produce higher values. This effect remains unexplained. In regard to the fluff, Figure 4 shows that higher values of t_a are obtained at 5 and 15 mole % than at 10 mole %. The 5 mole % level appears best for t_a ; however, the volatility at this level is too high for coating. Pellets from the 10 mole % NH_3 treatment give improved t_a and, after pumping, lower volatility. Pellets made from the 15 mole % NH_3 -treated fluff also show improved stability. After extended pumping these pellets had a lower volatility than the 10 mole % pellets; however, the volatility is still too high for coating. In addition, the stability tests show that pumping is decreasing the stability.

Figure 5

Variation of t_a with NH_3 Treatment Level (C)



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From our results it is obvious that the ammonia treatment of water-treated NP is a very complicated process. In addition to the complication of the gas phase reaction, there appears to be a number of control factors that make this dual treatment unpractical. There is no simple way of determining the extent of reaction of the stabilizer. Also, side reactions may be involved. The unexplained variation with the temperature of the treatment and the effect of pelletizing indicate that this process is not readily controlled. Thus, there appears to be little incentive for further study of this technique.

3. Other Treatments Unsuccessful

(C) Several other attempts were made to modify water-treated NP. However, the results of these attempts were not promising. Thus, modification of water-treated NP for volatility reduction remains a problem in the utilization of water-treated NP.

a. BF₃ Treatment Uneffective

(C) During the water treatment optimization studies, BF₃ was added to 10 mole % water-treated NP. The results of this treatment (Section IV) showed that it did not improve the stability of the water-treated NP.

b. Trimethylamine Treatment Detrimental

(C) In addition to ammonia treatment, we treated 10 mole % water-treated NP with 10 mole % of trimethylamine. This would give a comparison with ammonia treatment and also show the effect of changing the size of the cation in the stabilizer. After 6 hours of pumping at room temperature, the treated material was subjected to stability testing. The gas evolution was very high, 2 std. cc./g./100 hrs., and the decomposition accelerated in less than 100 hrs. Thus, treatment with amines is detrimental.

c. Iodine Pentoxide Partially Effective

(C) Another modification of water-stabilized NP involved the addition of an anhydride. Reaction of the anhydride with the hydronium perchlorate should effectively lower the volatility. However, the effect of this reaction on the stability was uncertain. To test this we prepared mixtures which contained 5 and 10 wt. % iodine pentoxide, using 10 mole % water-treated NP. After the mixtures were pumped 6 hours, stability tests were made.

| Sample* | 60°C Stability | | t _a |
|--|----------------------|----------------------|----------------|
| | Std. cc./g./100 hrs. | Std. cc./g./400 hrs. | |
| 5 wt. % I ₂ O ₅ | 1.18 | 2.34 | 500 |
| 10 wt. % I ₂ O ₅ | 0.68 | 1.64 | >600 |

* Mixture made with 10 mole % H₂O-treated NP.

The high values of t_a indicate that some retention of the stabilizer was achieved. Thus, this approach gives some reduction in volatility. However, the high gas evolution at the lower level indicates that a high level of additive is necessary. Thus, this type of stabilization appears unattractive. In addition, tests with untreated NP and iodine pentoxide have shown more beneficial results. This is described in the next section.

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VIII. ADDITIVE SCREENING STUDY

(U) During the course of the NP studies, we conducted a screening program in search of other additives which stabilize NP. This study was partly empirical and partly guided by our thoughts on NP stabilization at the time. Since the study extended over the entire period of the contract, it reflects periodic changes in our views on NP stabilization. Although some generalizations on the effect of various additives can be made, we have not found any uniform theory for additive selection. In fact, some of the positive results still cannot be explained.

A. FEW ADDITIVES IMPROVE STABILITY

(U) An effective stabilizer for NP should give both a high value of t_a and a low value of gas evolution when mixed with NP in small amounts. We found few cases which approached these requirements.

1. I₂O₅ Effective, But Too Much Required

(C) Iodine pentoxide was one of the few materials which gave both increased t_a and low values of evolved gas. However, the amount needed to give reasonable values of t_a results in significant losses in the energy content of the mixture. We have no explanation as to how this stabilizer acts. Unfortunately, it was discovered late in the study and further investigation was not possible.

| Additive | Level | 60°C Stability | | |
|-------------------------------|----------|----------------------|----------------------|--------------|
| | | Std. cc./g./100 hrs. | Std. cc./g./400 hrs. | t_a , hrs. |
| I ₂ O ₅ | 1 wt. % | 0.55 | -- | 100 |
| I ₂ O ₅ | 5 wt. % | 0.59 | 1.22 | 460 |
| I ₂ O ₅ | 10 wt. % | 0.62 | 1.10 | 600 |

2. Fluorine Treatment Also Increases t_a

(C) We also discovered late in the project that a mild treatment with fluorine gas increases t_a . The magnitude of the effect is not as great as water treatment, but then the level of treatment is uncertain. Also this stabilization may indicate a different mechanism for stabilization. Recently, free radicals have been found in NP (16). Thus, fluorine may scavenge these free radicals and thereby give greater stability. An alternate possibility is that fluorine may oxidize and remove the carbonaceous impurities which produce the carbon dioxide previously observed in the evolved gas. Since little fluorine is likely to remain in the treated NP, a less volatile additive with similar properties would be more effective.

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| Treatment* | Pumping Period | 60°C Stability | | |
|--------------------------|----------------|----------------------|----------------------|-----------------------|
| | | Std. cc./g./100 hrs. | Std. cc./g./400 hrs. | t _a , hrs. |
| None | 10 min. | 0.58 | -- | 100 |
| 30-45°C, 0.5 mmoles/min. | 5 min. | 0.32, 0.34 | 1.28, 1.54 | 320 |
| 0°C, 0.2 mmoles/min. | 10 min. | 0.70 | 1.24 | 350 |
| Pellets of above | 10 min. | 0.34 | -- | 150 |
| | 3 hrs. | 0.36 | -- | 150 |

* Treatment with 20% F₂ in N₂ for a period of 40-45 minutes.

3. Some Acids Increase t_a

(C) Screening tests on a number of acids showed increases in t_a, but also usually gave higher gas evolution. Considering the composition of the effective acids, we believe that they probably represent a modification of water treatment. Since the addition of a low volatile liquid to NP involves mixing problems, it is doubtful that these additives have any real value. An exception to this is periodic acid, H₅IO₆. This crystalline hydrate is the only crystalline hydrate that we have found effective in stabilizing NP. This might provide a convenient means of adding water to NP; however, the energy loss and potential volatility problem make this unattractive.

| Additive | Treatment Level | 60°C Stability | | |
|--------------------------------------|-------------------|----------------------|----------------------|-----------------------|
| | | Std. cc./g./100 hrs. | Std. cc./g./400 hrs. | t _a * hrs. |
| H ₅ IO ₆ | 1 wt. % | 0.80 | 1.56 | 740 |
| | 5 wt. % | 0.60 | 1.34 | >970 |
| | 10 wt. % | 0.58 | 1.38 | >970 |
| HClO ₄ •2H ₂ O | 0.25 cc./g. of NP | 0.86** | 1.8** | >500 |
| | | 2.74 | -- | >300 |
| | 0.1 cc./2 g. | 1.5** | 2.40** | >690 |
| | | 1.6 | 2.42 | >690 |
| H ₃ PO ₄ | 0.53 cc./2.5 g. | 0.96, 0.90 | 3.0, 2.94 | >500 |
| | | None | 0.72, 0.82 | -- |

* Greater than signs indicate no acceleration evident when test was discontinued.

** VTS sample evacuated at -196°C.

B. MANY ADDITIVES ARE DETRIMENTAL TO NP

(U) Many of the additives tested resulted in excessive gas evolution. In some cases t_a was reduced and in others the effect on t_a was obscured by the gas evolution. In either case, the additive definitely is not a stabilizer.

1. Inorganic Salts Usually Cause Excess Gas Evolution

(U) During the project a number of salts were tested for various reasons. However, the results of these tests clearly showed that ionic salts generally lead to excessive gas evolution. It is possible that a salt with the right crystal structure could lead to

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stabilization when incorporated into the crystal structure of NP. However, it is doubtful that such a condition could arise out of simple mixing of the dry solids. Thus, salts show no potential as additive stabilizers. This agrees with our previous findings on NaBF_4 , NaF and other salts.

| Additive | Level | 60°C Stability | |
|-----------------------------------|-----------------|----------------------|--------------|
| | | Std. cc./g./100 hrs. | t_g , hrs. |
| LiF | .1 g./0.5 g. NP | (> 4. in 40 hrs.) | -- |
| $\text{Mg}(\text{ClO}_4)_2$ | .1 g./0.5 g. | 1.16 | < 50 |
| NaIO_4 | 1 wt. % | > 3 | < 60 |
| | 5 wt. % | > 3 | < 60 |
| | 10 wt. % | > 3 | < 60 |
| $\text{K}_2\text{Cr}_2\text{O}_7$ | .005/0.5 g. | > 4 | < 50 |

2. Some Solid Acids Give High Gas Evolution

(C) Early in the water treatment study, tests were made on a few compounds to determine if solid acids would be effective. In contrast to the effect of some of the mineral acids, these compounds gave excessive gas evolution.

| Additive | Level | 60 °C Stability | |
|--------------------------|--------------------|----------------------|--------------|
| | | Std. cc./g./100 hrs. | t_g , hrs. |
| H_2SiO_3 | 0.0722/0.9 g. NP | -- | 50 |
| CF_3COOH | 0.0727 cc./1.25 g. | 1.41, 1.61 | 100 |
| $\text{Al}(\text{OH})_3$ | 0.0302 g./1 g. | -- | 50 |
| HIO_3 | 1 wt. % | 1.1 | < 100 |
| | 5 wt. % | > 3.0 | < 60 |
| | 10 wt. % | > 4.0 | < 60 |
| (Pyrophosphoric Acid) | .15 cc./2.5 g. | (1 cc. in 20 hrs.) | < 50 |

3. Many Oxides Give High Gas Evolution

(U) Early in the program a number of oxides were tested. Originally these oxides seemed attractive because they could scavenge residual water and would be resistant to oxidation. Since ultra-dry is not the solution to NP stability, it is not surprising that these additives proved to be ineffective. Of those oxides tested, V_2O_5 had little effect and Cr_2O_3 gave an increase in t_g . The rest gave excessive gassing or low values of t_g .

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| <u>Additive</u> | <u>Level</u> | <u>60°C Stability</u> | |
|--------------------------------|--------------------|-----------------------------|-----------------------|
| | | <u>Std. cc./g./100 hrs.</u> | <u>t₉₀</u> |
| MgO | .1 g./0.5 g. of NP | (1 in 1 hr.) | -- |
| P ₂ O ₅ | 0.05 g./0.5 g. | -- | 50 |
| | .01 g./0.5 g. | -- | 50 |
| B ₂ O ₃ | .1 g./0.5 g. | (>4 in 20 hrs.) | -- |
| CuO | .1 g./0.5 g. | -- | 50 |
| Alumina | .1 g./0.5 g. | -- | 50 |
| AgO | .1 g./0.5 g. | (>4 in 5 hrs.) | -- |
| V ₂ O ₅ | .1 g./0.5 g. | .82 | 100 |
| Cr ₂ O ₃ | .007 g./0.5 g. | 1.32 | 190 |

4. Fuels Are Bad

(U) Included in our screening program were some materials that could be classed as fuels. Most of these materials have some degree of oxidation resistance. However, our experience indicates that even a poor fuel reacts with NP at 60°C.

| <u>Additive</u> | <u>Level</u> | <u>60°C Stability</u> | |
|---|-------------------------------|-----------------------------|----------------------------|
| | | <u>Std. cc./g./100 hrs.</u> | <u>t₉₀ hrs.</u> |
| H ₂ C ₂ O ₄ •2H ₂ O | 0.016/g./0.5 g. of NP | 2.6, 2.6 | -- |
| C ₆ F ₅ OH | ----- Burned on contact ----- | | -- |
| Graphite | .002 g./0.5 g. | >4.0 | -- |
| Silicone grease | Coating on pellet | Exploded | -- |
| I ₂ | 1 wt. % | >4.0 in 90 hrs. | -- |
| Cobalt Phthalocyanine | 1 wt. % | >3.0 in 16 hrs. | -- |
| (CH ₃) ₄ NIO ₄ | 5 wt. % | >3.0 in 60 hrs. | -- |

5. Nitrogen Oxides Cause Gas Evolution

Although they are not really consider as additives, tests were made on nitrogen oxides to determine the effect of these gases under our test conditions. Although N₂O had little effect, both NO and NO₂ caused high gas evolution.

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| <u>Additive</u> | <u>Level</u> | <u>60°C Stability</u> | |
|------------------|----------------|-----------------------------|-----------------------------|
| | | <u>Std. cc./g./100 hrs.</u> | <u>t₉₀, hrs.</u> |
| N ₂ O | 12 mm pressure | .68 | 110 |
| NO | 12 mm | (>3 in 50 hrs.) | --- |
| NO | 17 mm | (>4 in 22 hrs.) | --- |

C. SOME MATERIALS GIVE LITTLE EFFECT

(U) Some of the effects noted in the previous subsection were small and probably reflect changes in the water content of the NP. Some tests were made on silica gel and Cab-o-sil, but the results were erratic and it was uncertain just what effect these materials had. In conjunction with our precoating studies, tests were made with Kel-F waxes. These tests showed no significant changes in gas evolution.

| <u>Sample</u> | <u>60°C Stability</u> | | |
|--------------------------|-----------------------------|-----------------------------|-----------------------------|
| | <u>Std. cc./g./100 hrs.</u> | <u>Std. cc./g./400 hrs.</u> | <u>t₉₀, hrs.</u> |
| Uncoated Pellets* | 0.92, 0.78 | 1.06, 1.63 | >500 |
| Kel-F 40 coated pellets | 0.78, 0.78 | 1.32, 1.58 | >500 |
| Kel-F 200 coated pellets | 0.98, 0.70 | 1.64, 1.30 | >500 |

* Pellets made by Thiokol.

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IX. CRYSTAL MODIFICATION ATTEMPTS

During the latter part of the current study, we attempted to change the crystal structure on the surface of the NP. In this approach, we hoped to stabilize NP in a manner similar to that of water-treated NP without use of a volatile stabilizer. Incorporation of suitable ions in the structure of the NP might deactivate the surface sites which are the initial sites of the decomposition.

A. TETRAFLUOROBORATE SALTS SELECTED

Two tetrafluoroborate salts were selected to test this hypothesis of NP stabilization. The tetrafluoroborate ion is similar to the perchlorate ion except that it shows little tendency to interact with nitronium ions. Crystal studies on NP show that the NO_2^+ and ClO_4^- are slightly distorted (14); but, studies on nitronium tetrafluoroborate (18) indicate little interaction occurred. Therefore, BF_4^- looked attractive.

The studies on water stabilization of NP indicated that the interaction of H_3O^+ ions in the NP crystal structure is an important factor in the resulting stabilization. However, this ion also causes volatility problems. Since the NH_4^+ ion shows crystal properties similar to the H_3O^+ ion, it also appeared attractive. Furthermore, it could interact with the perchlorate ion by hydrogen-bonding and thus decrease the distortion of the NO_2^+ ions. Therefore, NO_2BF_4 and NH_4BF_4 were selected as model salts for the crystal modification.

B. RESULTS NOT ENCOURAGING

The ammonium tetrafluoroborate was prepared by reaction of ammonium fluoride with boron trifluoride. After sublimation, the resulting ammonium tetrafluoroborate was mixed with NP and the mixture slurried in nitromethane. The solvent was removed under vacuum and the mixture tested. At 60°C excessive gassing was observed.

Similarly, nitronium tetrafluoroborate was prepared from nitronium fluoride and boron trifluoride. Several variations were carried out which included in situ preparation on the NP. However, these attempts all resulted in excessive gas evolution during stability testing. Finally, nitronium tetrafluoroborate itself was tested. This, too, gave high gas evolution.

| Modifier | Condition | 60°C Stability | |
|---|---|----------------------|--------------|
| | | Std. cc./g./100 hrs. | t_a , hrs. |
| NH_4BF_4 | 39 wt.%, slurried in CH_3NO_2 | (>4 in 16 hrs.) | --- |
| NO_2BF_4 | prepared <u>in situ</u> in CH_3NO_2 | >3.0 | --- |
| NO_2BF_4 | prepared <u>in situ</u> without solvent | >4.0 | <50 |
| (neat NO_2BF_4 prepared in CH_3NO_2) | | 3.1 | >350 |
| (neat NO_2BF_4 prepared without solvent) | | (>4.0 in 17 hrs.) | --- |

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C. BETTER SOLVENT NEEDED

Although nitronium tetrafluoroborate no longer looks attractive as a crystal modifier, the use of ammonium tetrafluoroborate, or ammonium perchlorate, cannot be readily dismissed. The critical facet of this approach is the achievement of a mixed crystal system. This requires intimate contacting between the NP and the modifier. Unfortunately, a good solvent for this purpose is not known. NP is partially soluble in nitromethane but also appears to react with it. In our experiments, the nitromethane turned yellow after contact with NP. Purification of the nitromethane failed to eliminate this reaction. This reaction appears detrimental to the NP. Even 10 mole % water-treated NP showed a loss in stability (gas evolution > 3 std. cc./g. after 18 hrs. at 60°C) after contact with nitromethane. Further work on crystal modifiers would be attractive if a solvent compatible with NP was found.

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X. SYNTHESIS STUDY

(U) A limited synthesis study was made with a small laboratory synthesis unit which was available from the previous ARPA-sponsored work. The unit was originally designed to produce ultra-dry NP from NO_2 , ClO_2 and ozone, but during this study the unit was modified to improve purity.

A. ULTRA-PURE NP WAS OUR OBJECTIVE

(C) Initially, we attempted to prepare ultra-dry NP as a reference material for our stability tests. However, analysis showed our sample contained 0.019 wt.% hydrogen. When the relationship of water content to NP stability was established, this approach was dropped. Instead, we attempted to produce NP of higher purity. Mass spectral analysis of the decomposition gases had revealed a small amount of carbon dioxide. Elimination of this component from the decomposition products would give a significant reduction in the gas evolution. Also, we hoped that carbon-free NP might show exceptional stability. Therefore, the unit was modified to reduce exposure to CO_2 during synthesis.

B. SYNTHESIS RESULTS DISCOURAGING

(U) All the NP produced in this study exhibited poor stability. A typical sample gave 0.9 std. cc./g. after only 20 hrs. at 60°C . Before modification of the synthesis unit, the decomposition gases from the NP samples contained 61.4% CO_2 . We believed that this CO_2 was incorporated in the NP during synthesis. Probably, CO_2 was being adsorbed from the air stream used to make the ozone. To circumvent this, we installed an efficient CO_2 adsorber in the air stream. Tests showed no CO_2 in the scrubbed air.

1. CO_2 Still Present in Decomposition Gases

(U) NP prepared after modification to remove CO_2 still showed considerable gas evolution in stability tests. The CO_2 content of these gases was reduced to 41% but not eliminated. The source of this CO_2 is still uncertain. Possibly it arises from the oxidation of some carbon source in the unit.

2. NP Has Low Bulk Density

(C) The NP which was synthesized in our lab unit also had a very low bulk density. Apparently this was a consequence of the conditions used in our unit -- low partial pressures and room temperatures. Variation of the flow rates of the various synthesis streams failed to produce any marked improvement in this property. The very fine particle size is also likely to be the cause of the poor stability. The decomposition is initiated on the surface of the NP. Thus, the larger surface area associated with the fine particles results in a greater decomposition rate. Callery has reported (17) a similar effect of lower particle size and greater gas evolution for NP produced at temperatures below their normal synthesis condition. Therefore, the particle size effect appears to be more important than ultra purity.

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XI. MISCELLANEOUS EXPERIMENTS

(C) In order to establish a relationship between the results obtained in our labs with those at Union Carbide, tests were made by us on samples received from them. The first sample tested was some pellets originally made by Thiokol. These pellets were used by Union Carbide in their "Reta" coating program. Our test showed that these pellets had a proton content of 0.306 wt.% and a range of 0.66 to 0.92 std. cc./g./100 hrs. at 60°C. The value of t_g was >500 hrs. Oddly enough, the crushed pellets gave greater gas evolution at 60°C (>3.8 std. cc./g. in 50 hrs.)

Later in the program we received a sample of "Reta" coated NP pellets designated "7703-66" by Union Carbide. These were similar pellets made by Thiokol which has been coated by Union Carbide. The coating consisted of the following: (1) Kel-F 40/200 wax mixture, (2) magnesium oxide, and (3) two Reta layers. The gas evolution for the material was the lowest that we have observed; however, the value of t_g ranged from 350 to 500. After the samples showed accelerated decomposition, the pellets were exposed to atmospheric air. After standing overnight, only 11 to 33% of the pellets showed signs of hydrolysis. This indicates that only a small number of the pellets had disrupted or incomplete coatings at the conclusion of the test. Thus, small improvements in stability and coating should give a marked increase in the stability results.

| Sample | 60°C Stability | | |
|-------------------------------|----------------------|----------------------|-------|
| | Std. cc./g./100 hrs. | Std./cc./g./400 hrs. | t_g |
| Reta coated | 0.20 | 0.46 | 400 |
| Reta coated (Hg contaminated) | 0.12 | 0.62 | 350 |
| Reta coating | 0.22 | 0.40 | 500 |

A sample of 1/8 inch pellets made from 10 mole % water-treated NP was delivered to Union Carbide. An attempt was made to coat this material with a "Reta" material. Unfortunately, difficulty was encountered in evacuation and the coating was attempted at 100 microns pressure rather than the usual pressure of 20 microns. As soon as coating was started, the pressure rose suddenly and the monomer backed up into the furnace and decomposed.

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XII. CONCLUSIONS AND RECOMMENDATIONS

(C) Stabilization of NP by BF_3 has limited utility. Reduction of gas evolution is apparently achieved by reaction of BF_3 with evolved nitrogen oxides. BF_3 is consumed and has little effect on the onset of the accelerated reaction. Nevertheless, some benefit has been achieved when used with "Reta" coating.

(C) Ultra-dry NP does not appear to be the answer to the stability problem. Although dried samples show low gas evolution at 60°C , the induction period before accelerated decomposition is short. In contrast, water treatment of NP gives a marked increase in the time for the onset of accelerated decomposition (t_a). 10 mole % H_2O treatment (1.23 wt.%) is the optimum treatment. This yields t_a values greater than 1000 hrs. at 60°C and gives low gas evolution (0.5 std. cc./g./100 hrs. at 60°C). Unfortunately, the stabilizer is volatile and can be removed. Therefore, water-treated NP must be coated to be useful.

(C) Kel-F waxes are not strong enough to be used as a precoating for water-treated NP prior to "Reta" coating. The volatility of the stabilizer is sufficient to disrupt the wax film. Therefore, some other method of volatility control is needed. A dual treatment of water followed by ammonia has given reduced volatility; but, variation in results makes control of the process doubtful.

(C) Screening studies failed to uncover any practical additives for stabilization. Two additives (fluorine and iodine pentoxide) gave improvements that might merit further study. Mechanism studies might reveal new methods for stabilization. Also, the effect of interhalides on NP might be informative.

(C) We failed to achieve any stabilization in attempts to modify the surface crystal structure of NP with NO_2BF_4 and NH_4BF_4 . However, this approach requires a compatible solvent. If a solvent that is compatible with NP is discovered, this approach should be investigated further.

(C) Synthesis conditions of NP affect the stability. Those factors which influence particle size are most important. Very small particles are less stable than larger ones. There is still a need to eliminate the source of CO_2 observed in the stability tests during the induction period.

(C) These studies have shown that under certain conditions the stability of NP can be improved. Particularly, the accelerated decomposition can be greatly retarded. This suggests that NP is not inherently unstable. However, the established relationship between water and NP clearly indicates that any stabilized NP will require protection from moisture even at very low levels. Elimination of all gas evolution during the induction period at 60°C requires the elimination of the source of the carbon dioxide observed in the decomposition gases. Further, development of a non-volatile stabilizer seems unlikely without the discovery of a compatible solvent.

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APPENDIX I

STABILITY TEST METHODS

(U) Stability tests involved several different types of apparatus and procedures. The majority of the tests were made in the standard apparatus shown in Figure 6. This apparatus was originally designed by Dr. J. A. Brown of Esso Research and Engineering Company for use in Vacuum Thermal Stability tests during the ARPA-sponsored work. In general, the tubes were cleaned, dried, evacuated, then flamed; mercury was added and boiled under vacuum to remove any air. The tubes were loaded with the NP samples in a dry-box maintained below 1 ppm of H₂O and usually operated at 0.5 ppm H₂O. The box utilized air that was dried with a Gilbarco Heatless Dryer. The moisture content was monitored with a Gilbarco Sorption Hydrrometer.

(U) After the tubes were loaded, they were evacuated for 10 minutes and placed in a 60° oven. For readings, the tubes were normally removed from the oven and cooled to room temperature. Gas evolution in std. cc./g. were calculated from pressure, volume (approx. 9 cc.) and temperature using the ideal gas law. Time corrections were made for cooling tubes, taking readings and reheating the sample.

(U) A second type of apparatus used was a modification of the first in which a teflon needle valve was located between the manometer and the stability tube (point A in Figure 6). With this apparatus we could minimize the contact between the decomposition gases and mercury vapor. In practice, the opening and closing of this valve eventually caused leakage when readings were taken; therefore, this apparatus was not used to any great extent.

(U) For mass spectral studies, the apparatus in Figure 7 was used. This tube was filled in the dry-box and closed with a stopcock attached to the proper ball joint. The unit was then connected to a vacuum system. After evacuation the tube was sealed off below the ball joint. The tube was then placed in an oven. After heating for the desired time, the unit was attached to a mass spectrometer and opened by means of the break seal.

(U) The fourth type of apparatus was another all glass unit (Figure 8) which utilized a glass membrane as a null indicator. By balancing the pressure on the reference side of the membrane to match that on the sample side, the decomposition of the NP can be followed without exposure to mercury. Loading of the apparatus was similar to the sealed tube noted above, but a little more tedious. These glass diaphragm units were purchased from Reaction Motors at Denville, New Jersey.

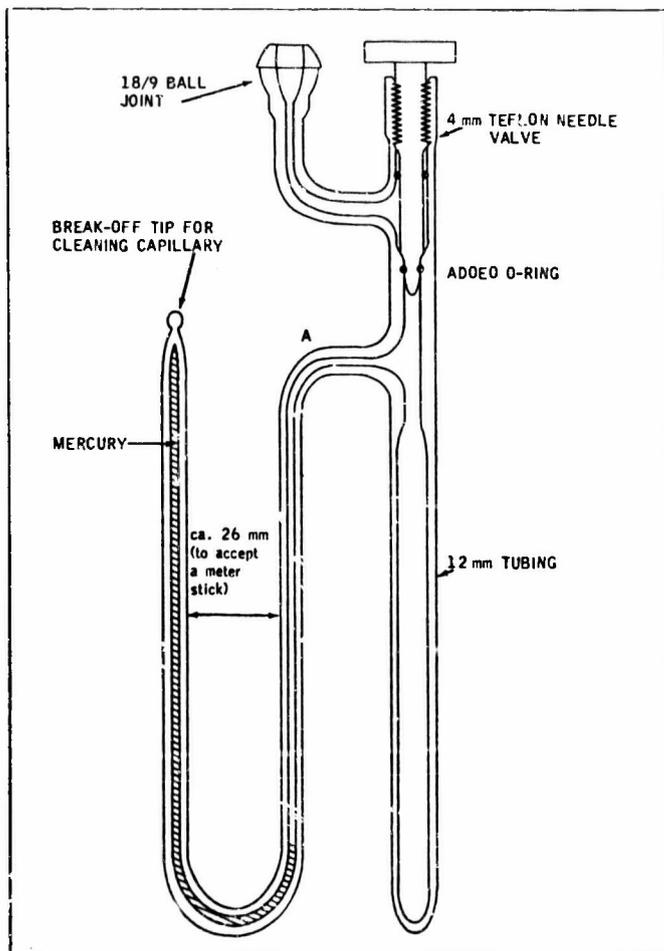
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Figure 6

Vacuum Thermal Stability Apparatus (U)



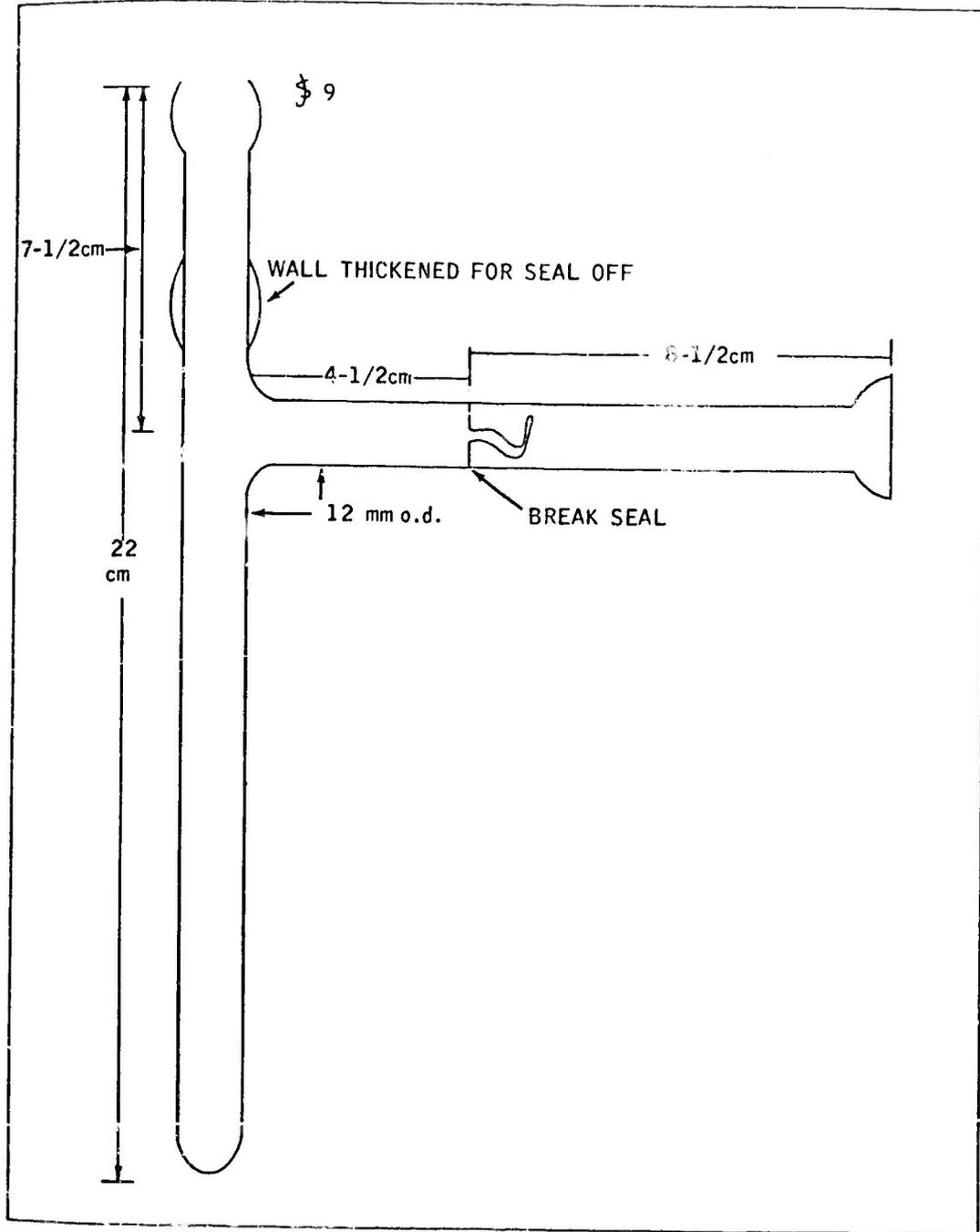
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Figure 7

Sealed Tube Stability Apparatus (U)



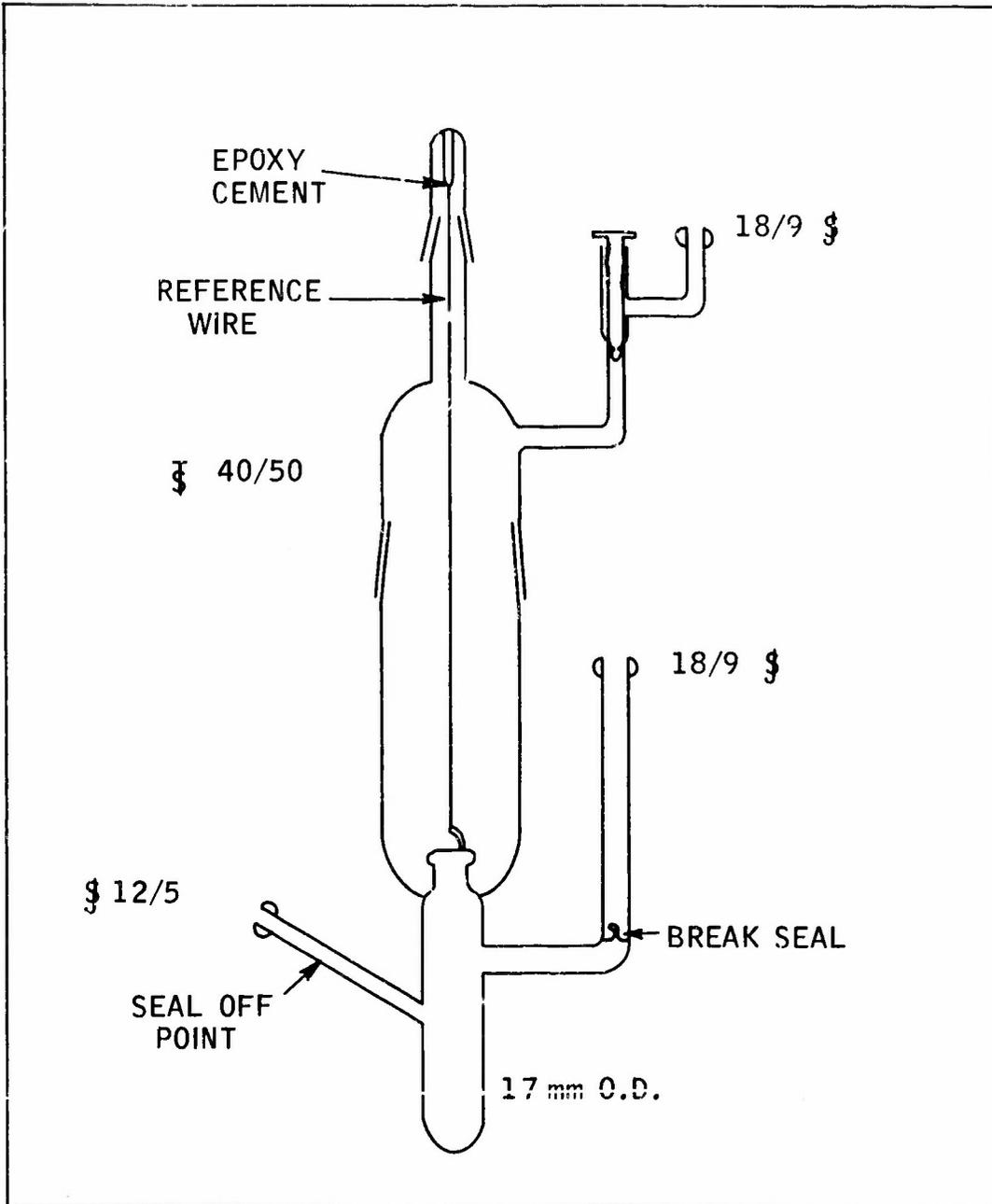
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Figure 8

Mercury-free Stability Apparatus (U)



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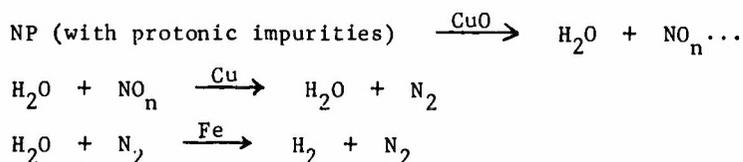
APPENDIX II

PROTON ANALYSIS OF NITRONIUM PERCHLORATE

(U) The following method of trace proton analysis developed largely under ARPA sponsored Army Contract No. DA-30-069-ORD-2487 was finalized under Air Force Contract No. AF-04-(611)-10538 and the fully developed procedure is being reported here.

A. INTRODUCTION

(U) This method comprises a combustion-gas chromatography technique (19,20) for analysis of hydrogen in the 50-1000 ppm range. In principle, the sample and its products are reacted with the combustion tube packing which consists of zones of hot copper oxide, copper, silver and iron, to form hydrogen and nitrogen gas according to the following simplified equations.



The hydrogen gas formed is measured in a calibrated thermal conductivity detector. Initial analysis of two samples of commercial NP with a level of about 0.02 to 0.03 wt. % hydrogen gave an estimated precision of $\pm 0.004\%$.*

B. APPARATUS

(U) 1. Dry Box. An air dry box equipped with a Gilbarco Heatless Dryer was used in this procedure. This box was maintained at a moisture content of 0.5 ppm or less and was monitored with a Gilbarco Sorption Hydrometer.

(U) 2. Combustion Apparatus. A diagram of the apparatus is shown in Figure 9. The combustion tube is heated by three multiple furnace units: type 123-1, 4 inch size, obtained from the Deni-Duty Electric Co., Milwaukee, Wisconsin. The furnace units over the packed zones are maintained at $725^\circ\text{C} \pm 10^\circ\text{C}$.

(U) The by-pass line consists of a stainless steel tube of approximately the same diameter as the combustion tube. It is packed with copper turnings equivalent to the quantity of total packing in the combustion tube. The purpose of this hot by-pass system is to balance this gas stream with the sample gas stream thus giving smoother detector operation.

(U) The combustion and by-pass connections are made with Swagelok fittings.

* This method gives total proton content. Previous NMR analysis on the 0.02 wt. % H sample gave no signal indicating less than 0.006 wt. % of hydrogen. However, the NMR may not be sensitive to all the hydrogen.

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(U) Argon, the sieve-dried carrier gas (100 cc./min.), is directed by means of solenoid valves into either of two possible flow systems, i.e., (1) through the combustion tube, or (2) through the by-pass system. During the sample combustion stage no gas flows through the combustion tube. The flow of gas during this stage is through the by-pass system and into the gas chromatography unit. Upon completion of the combustion stage or cycle, all the argon is directed through the combustion tube and then into the gas chromatography unit. The use of the balanced by-pass tube system allows the base line from the gas chromatography detector to remain steady during the gas switching.

(U) 3. Combustion Tube Dry Box. A small dry box at the entrance end of the combustion tube offers protection against uptake of water from the atmosphere. The dry box is supplied with exhaust argon from the gas chromatography unit. It is constructed from 3/8" Lucite and the dimensions are 18" x 8" x 10". This dry box is also used to keep the combustion boat pusher rod and gloves reasonably dry.

(U) 4. Combustion Tube and Packing. See Figure 10.

(U) 5. Combustion Boats. Micro, Platinum.

(U) 6. Gas Chromatography Unit. Gow-Mac Power Supply Unit, Model 405-C1, a micro thermal conductivity cell, and the chromatographic column is a stainless steel tube 3/16" I.D., 72 inches long, packed with Molecular Sieve Type 5A (21) (40-60 mesh). An argon flow rate of 100 cc./min. is used and the column and detector are maintained at room temperature.

(U) 7. Spex Mixer/Mill. Catalog No. 5000, available from Spex Industries, Inc., Scotch Plains, New Jersey.

(U) 8. Stainless Steel Vial and Ball.

(U) 9. Weighing Pig. Micro, Fischer-Porter Co., Warminster, Pennsylvania, Catalog No. 179-952.

C. REAGENTS

(U) The following reagents were used:

1. Copper Oxide, wire form, reagent grade, ignited at 800°C.
2. Copper Turnings, purified grade, chloroform and acetone washed.
3. Silver Wool, chloroform and acetone washed.
4. Quartz Wool.
5. Iron Wire, reagent grade, 0.009" diameter. The wire is cut in 1/8" to 1/4" lengths, chloroform and acetone washed.
6. Molecular Sieve, type 5A, 40-60 mesh.
7. Dinitrobenzoic Acid. CP grade.
8. Ammonium Perchlorate.
9. Copper Oxide-Dinitrobenzoic Acid Blend. Weigh a suitable quantity of the standard and 1 to 1-1/2 grams of dry powdered copper oxide into a stainless steel vial containing a steel ball. The vial is capped and the mixture blended by means of a Spex Mixer/Mill. Blend intermittently for about 90 seconds.
10. Copper Oxide-Ammonium Perchlorate Blend, prepared in same manner mentioned above.

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D. CALIBRATION

(U) 1. Weights of calibration standards were chosen to give a calibration curve ranging between 2 and 6 μ g. hydrogen (Figure 11).

NOTE: The samples are transported to and from the weighing and combustion areas in a desiccator containing P₂O₅ and all sampling is performed in the described dry box.

(U) 2. The pyrolysis zone of the combustion tube is cooled with dry ice to avoid premature decomposition. It is important that the rest of the combustion tube not be cooled enough to cause condensation of any moisture admitted during the sample boat insertion step. The cooling is best accomplished by placing small pieces of dry ice against the by-pass tube under the sample zone.

(U) 3. Close off the flow of argon through the combustion tube by switching the solenoids to the by-pass line.

(U) 4. Open the Swagelok connection on the combustion tube and insert the sample boat with the aid of a wire boat pusher. It is advisable to wear some sort of gloves to minimize the effect of moisture during the handling of the "sample weighing pig" and boat push-rod. The push-rod and gloves should remain in the combustion tube dry box when not in use.

(U) 5. Close combustion tube and activate solenoids to direct the argon flow through the combustion tube. Permit the argon to sweep through for 10 minutes. During the sweep-out period the sample zone should be kept cool but not cold.

(U) 6. Activate solenoids to direct the argon flow through the by-pass line.

(U) 7. Close the sample furnace lid over the sample and turn on the heat. The temperature of this furnace should be brought up to 750°C.

(U) 8. Turn on the gas chromatograph recorder and select the range attenuation after a 30-minute combustion period.

(U) 9. Flame the cooler end of the combustion tube carefully by means of a small torch.

(U) 10. Activate the solenoids to direct the argon flow through the combustion tube into the gas chromatograph unit.

(U) 11. Measure the peak height of the hydrogen peak and plot peak height vs. μ g. hydrogen (Figure 11).

E. PROCEDURE

(U) 1. Accurately weigh approximately 20 mg. of NP into a platinum boat and cover with approximately 0.3 g. of dry powdered copper oxide. The amount of copper oxide used must be weighed and a blank correction made accordingly.

(U) 2. The combustion procedure is the same as that described for calibration.

(U) 3. The μ g.'s of hydrogen present in the sample is obtained from the hydrogen peak height on the calibration curve.

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F. RESULTS

(C) Initial results using this procedure gave the following results for two different sources of NP:

Proton Content of NP

| <u>Source Bottle</u> | <u>Wt. % H</u> | <u>"Wt. % H₂O"</u> |
|----------------------|--------------------------|-------------------------------|
| 276-6 | 0.023 | 0.21 |
| | .017 | 0.15 |
| | 0.017 | 0.15 |
| | 0.017 | 0.15 |
| | 0.025 ($\sigma=0.004$) | 0.23 |
| 276-138 | 0.030 | 0.27 |
| | 0.033 | 0.30 |

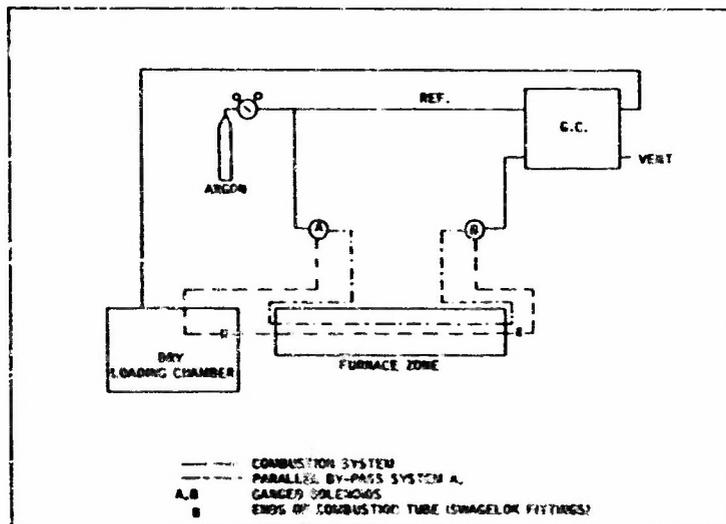
(C) These results were obtained over an eight day period. The variation in results were originally taken as an indication of the precision of the method. Later results have indicated that the reproducibility of the method may be better and that some of the variations are due to actual variations in the moisture content of the NP sample.

G. REMARKS

(U) The restriction of maintaining the dry box at 0.5 ppm H₂O and the standardization of the unit each day limits the output to one analysis per day. Although the life of the combustion tube packing is relatively long during the standardization runs, the packing has been changed for each NP analysis due to the high level of chlorine and nitrogen oxides and the resulting degradation of the column.

Figure 9

Schematic Diagram of Proton Analyser (U)



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Figure 10

Combustion Tube of Proton Analyser (U)

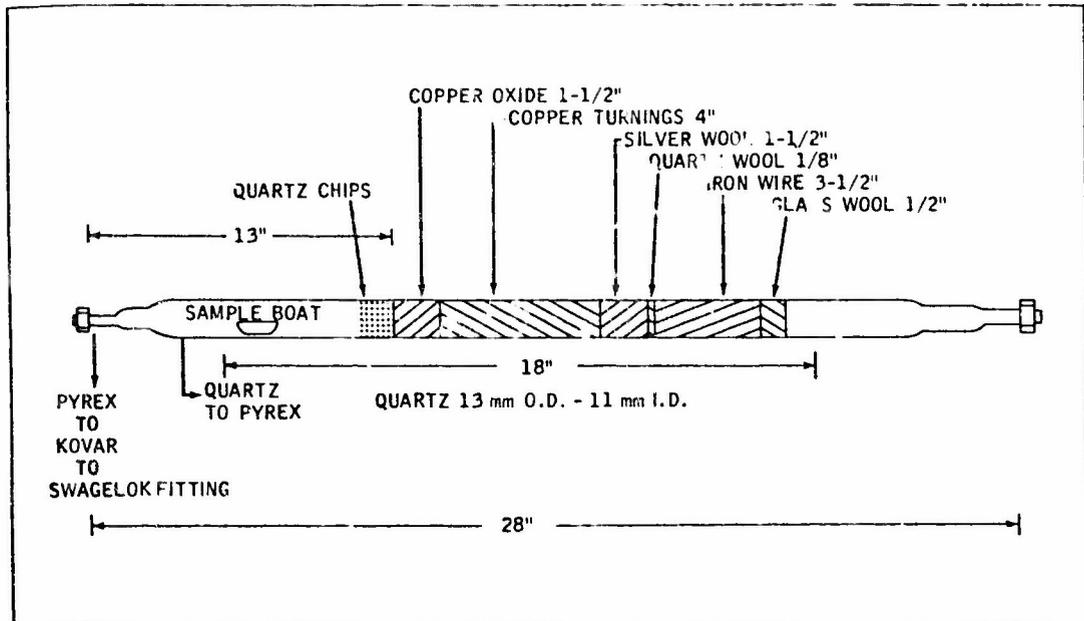
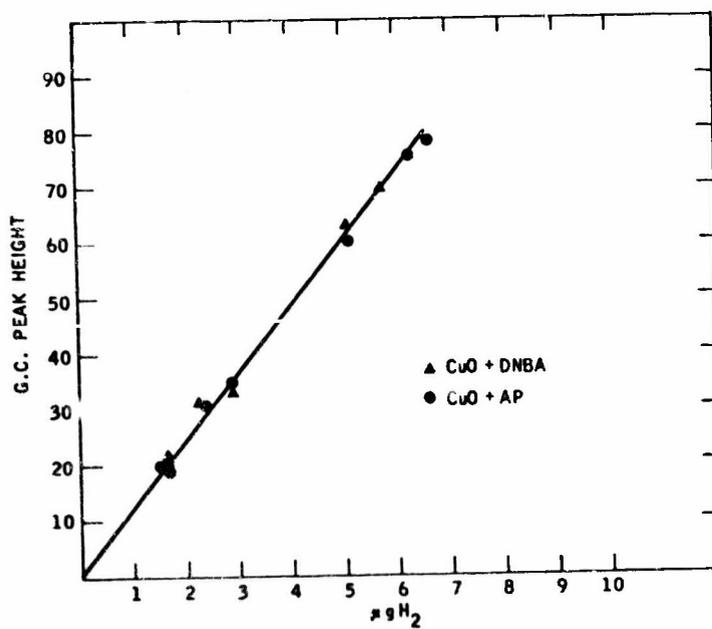


Figure 11

Calibration of Analyser (U)



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APPENDIX III

STANDARD WATER TREATMENT PROCEDURE

(C) The stabilization of NP by water treatment is, in part, dependent on the treatment procedure. Therefore, the standard procedure is detailed here for reference. The standard treatments have been conducted with 2.5 g. samples of NP. Each treatment is carried out on a vacuum rack in a 26 cc. bulb equipped with a Fischer-Porter valve. The reactor is loaded in the dry box (< 1 ppm. H_2O) and then evacuated on the vacuum line. The desired amount of water is placed in a similar bulb and attached to the vacuum line. The water bulb is cooled to $-196^\circ C$ and evacuated to remove air. After the water bulb is degassed, it is allowed to warm to room temperature. The NP bulb is partially immersed in a $-80^\circ C$ bath and the proper valves opened to allow the water vapor to flow into the NP bulb. The NP bulb is shaken with a vibrator to obtain efficient mixing. Most of the water must be condensed on the NP. Previous experiments have shown that reaction of condensed H_2O on the walls with small amounts of NP produced a non-volatile liquid. After the initial mixing, the temperature is cycled between 30° and $-80^\circ C$ (or $-196^\circ C$) to remove caked NP from the walls. Vibration of the reactor is continued throughout the experiment. When mixing is complete, the reactor is stored overnight in a $-80^\circ C$ bath which warmed to room temperature.

(C) If samples for stability testing are desired, the reaction vessel is returned to the dry-box. The NP is removed from the vessel, thoroughly mixed, and then loaded into the VTS tubes. Prior to stability testing, the VTS tubes are evacuated.

(C) There is an important consequence of this testing procedure. The handling of the treated material in the dry-box exposes the sample to a flowing, dry atmosphere. This allows some volatile component(s) produced during the reaction with H_2O to escape.

(C) In the 10 to 30 gram treatments, a larger vessel (60 cc.) was used and the water was introduced stepwise into the treatment bulb. To aid the removal of the volatile by-product, these larger batches were evacuated at the end of the treatment. In addition, small glass beads were usually introduced with the NP in order to aid mixing.

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