INTERIM TECHNICAL REPORT

TNX EVAPORATOR INCIDENT JANUARY 12, 1953

by

T. J. Colven, Jr., G. M. Nichols, T. H. Siddall

May 15, 1953

E. I. du Pont de Nemours & Co. (Inc.)
Explosives Department - Atomic Energy Division
Savannah River Laboratory
Augusta, Ga.

Contract AT(07-2)-1 with the United States
Atomic Energy Commission

1-3

ABSTRACT

The circumstances are described per-
taining to an explosion in a TNX evaporator
during the concentration of a uranyl nitrate-
nitric acid solution. TBP and Amsco diluent
were probably present in the evaporator
charge. A laboratory program involving small-
scale atmospheric and closed-vessel distil-
lations of various mixtures of UNH, HNO_3,
Amsco, TBP, and water indicate that an exo-
thermic reaction between TBP and UNH, or be-
tween TBP and HNO_3, or both, was responsible
for the explosion. The danger areas of temp-
erature, TBP concentration, pressure, and
heating rate are defined and recommendations
are made for safe evaporator operation.

TABLE OF CONTENTS

LIST OF FIGURES AND TABLES

INTRODUCTION

The TNX Semiworks (678-G Building, CMX Area) of the Savannah River Laboratory was built to obtain design and operating data in support of the 200 Area Separations Plant. An evaporator (similar to those to be used in the Building 221 canyon) had been installed and used since November 1951 to concentrate uranium solutions and to prepare process water. On January 12, 1953, while concentrating a uranyl nitrate-nitric acid solution, the evaporator was destroyed by an explosion.

This report (1) describes the circumstances pertaining to the operation of the evaporator at the time of the explosion, (2) reports the results of laboratory experiments designed to establish the process conditions under which self-sustaining reactions will and will not occur, (3) offers a tentative explanation of the evaporator explosion, and (4) makes recommendations to assure safe operation of the Purex process evaporators.

The experimental program is being continued in an effort to characterize the chemistry of these reactions. The results will be reported at a later date.

SUMMARY

At the time of the explosion, the TNX evaporator was being used to concentrate a uranyl nitrate-nitric acid-water mixture to a point where $\sim$ 50% of the HNO_3 would be removed as distillate. The force of the explosion ripped the evaporator pot into 6 major pieces, and damaged the bubble cap column to the extent that several of the trays were distorted. Damage to the building's steel framework was slight, but roofing and siding were extensively dislodged. Two minor injuries were sustained.

The fact that Amsco (a kerosene-like diluent for the tributyl phosphate extractant in the Purex process) was found in substantial quantities in the distillate was considered strong evidence that Amsco and tributyl phosphate (TBP) were present in the evaporator charge. Since these organic materials were suspected of being factors in causing the explosion, a laboratory program was initiated to determine the reactivity of these mixtures under various conditions.

Small-scale atmospheric distillations of various mixtures of UNH, HNO_3, Amsco, TBP, and water indicated the following:

TBP must be present to promote a noticeable exothermic reaction.

Mixtures of TBP, UNH, HNO_3, and water will react exothermically with varying degrees of vigor, depending on the heating rate and composition, but no reaction will take place at atmospheric pressure until enough water and HNO_3 have been distilled to permit the temperature of the charge to rise above 135° C   (78% UN).

The vigorousness of the reaction (observed by the extent of the sudden temperature rise) increases as the TBP/uranyl nitrate (UN) ratio is increased, but in no case was any reaction observed at a ratio below 0.12 under the conditions investigated.

Less TBP is required to promote a self-sustained reaction at a high heating rate (1°C/min) than at a low heating rate (0.1°C/min).

The system TBP/UNH/water will yield a self-sustained reaction, but when HNO_3 is present the reaction is more vigorous.

The system TBP/HNO_3/water will react with considerable violence if heated rapidly to temperature above 150°C.

SUMMARY (continued)

The following information was obtained from a series of experiments made in a closed pressure vessel using the same ingredients investigated in the atmospheric experiments and using the same vessel/charge volume ratio as existed in the TNX evaporator:

Self-sustained reactions were obtained with more dilute solutions than in the atmospheric experiments, but higher temperatures (possible under pressure) were required. For instance, at 47% UN, reaction was obtained at 195° C.

The pressure increases developed by the reactions varied from 150 psig at 0.06 TBP/UN to 1200 psig at 0.28 TBP/UN when the UN concentration was constant at 80%.

At a constant TBP/UN ratio of 0.21, the pressure increases developed by the reactions varied from 50 psig at 45% UN to 1300 psig at 85% UN.

Rates of pressure rise, observed with a piezoelectric gage, varied from 250 psi/sec to 1020 psi/sec; the higher rates were obtained with the higher peak pressures.

Very high pressure development rates were observed with TBP and HNO_3 (no UNH) in the pressure vessel tests.

Based on the information revealed by the two series of laboratory experiments, and the probable presence of TBP in the TNX evaporator, it is concluded that an exothermic reaction between TBP and UNH, or between TBP and HNO_3, or both, was responsible, either directly or indirectly, for the rupture of the evaporator.

The circumstances surrounding the evaporation of the charge in question indicate that the danger areas of temperature, TBP concentration, and heating rate defined in this report were probably attained.

RECOMMENDATIONS

In order to assure safe operation of the Purex process evaporators, TBP in excess of water-soluble quantities must not be permitted to enter the evaporators.

Any of the following additional safeguards can be employed where practical to decrease the potential hazard of the operation:

Hold temperature of the liquid in the evaporators below 125°C.

Use slow heating rates.

Design concentrating equipment with pressure relief mechanisms, such as large vents or rupture disks.

Design concentrating equipment for minimum hold-up to withstand sudden pressure increases.

FUTURE PROGRAM

The hazards testing program is being continued with the following objectives:

1. Evaluation of the hazards (if any) involved in evaporation of neutralized systems containing TBP.

2. Investigation of the actual chemistry of the reactions described in this report.

DETAILS

General

The TNX Semiworks program involved testing of equipment using Purex solutions: uranyl nitrate, nitric acid, and 30/70 TBP/Amsco. The evaporator (Figure I) was used primarily for concentrating the uranyl nitrate solutions to allow their re-use in semiworks studies.

At the time of the incident, a special series of evaporations was in progress to remove about 50% of the nitric acid from 1800 gallons of uranyl nitrate solution. Equipment size necessitated that the deacidification be carried out in several batches of approximately 500 gallons each and three batches had been successfully processed. The fourth and final charge consisted of the 70 gallon heel of the original solution plus 160 gallons of previously evaporated material which had been diluted with water. The additional 160 gallons were required to make a minimum evaporator charge.

Because the liquid temperature recorder was broken and since the required degree of concentration was beyond the range of the specific gravity recorder, the evaporation was being carried out for a specified length of time based on past experience. Five minutes prior to the scheduled completion of this fourth evaporation, a violent reaction took place with sufficient pressure to destroy the evaporator pot and cause extensive damage to the building.

The operator present at the time stated later that he heard a rumbling noise, and then observed orange-colored fumes evolving from the top of the column with a high-pitched roar. This observation is considered evidence that a reaction vigorous enough to produce copious quantities of gas or vapor was taking place. On the basis of previous experience, it was suspected that the reaction was accompanied by considerable frothing. This suspicion was confirmed when a later examination of the column bubble-trays revealed that the lower trays were at least partially plugged with solid material. This partial plugging of the column could well have facilitated a pressure build-up in the evaporator, prior to its rupture.

Due to its use in semiworks studies, all of the aqueous uranyl nitrate fed to the evaporator had at one time been in contact with solvent (30/70 TBP/Amsco). Although none of this organic solvent was thought to have been present in the feed, it was discovered, subsequent to the explosion, that Amsco diluent was present in the distillate catch tank. From the quantity of Amsco collected, and from phosphorous analysis of the evaporator residue, it was estimated that about 80 lbs. of tributyl phosphate (TBP) had been present in the evaporator charge. It was theorized that a reaction between uranyl nitrate

and organic material could have occurred in the evaporator. This theory is supported by reports in the literature of such runaway reactions. The odor of butyric acid, present after the explosion, was additional evidence of an oxidation reaction involving TBP.

An experimental program was initiated to determine whether a violent reaction could be produced under conditions similar to those now postulated to have existed at the time of the evaporator incident. The solutions tested were taken from TNX process tanks where possible and synthesized in other cases. Atmospheric and closed bomb tests were made on the various systems as follows:

Atmospheric	Bomb
UN-HNO$_3$-TBP	UN-HNO$_3$-TBP
HNO$_3$-TBP	HNO$_3$-TBP
UN-HNO$_3$-TBP/Amsco	
UN-TBP	

Experiments at Atmospheric Pressure

Small scale scouting tests were made in 20 mm test tubes heated in a sand bath. These tests were designed to give qualitative evidence as to whether a given system would produce a spontaneous reaction and at what temperature.

These preliminary scouting tests were run on 1-2 cc of various solutions involved in the incident. In further tests, about 10 ml of synthetic test solutions were charged to the test tubes. The systems were then heated in the sand bath and observations made of the liquid temperature, gas evolution, and foaming. In those cases where a spontaneous reaction took place, it was characterized by foaming, rapid evolution of oxides of nitrogen, and solidification of the residue. The results of these tests are shown in Table I.

The negative results in Runs 1 through 7 (Table I), can be attributed, for the most part, to the small amount of test solutions, i.e., a reaction could have taken place unnoticed. The removal of the butanol in Run 8 by distillation at $\sim$100°C prevented any organic-HNO$_3$ reaction. A possible slow reaction occurred in the 100-200°C range between HNO$_3$ and TBP in Run 9.

Runs 10 through 13, in which reactions were noted at $\sim$135°C, had 70% HNO$_3$, TBP, and a heavy metal (U and Th) nitrate salt in common. Run 10 indicated that the Amsco had been distilled from a UN-HNO$_3$-TBP/Amsco mixture at $\sim$110°C before

the rapid reaction took place at ~ 135°C.

More quantitative tests were run in a 125 cc distilling flask heated by an oil bath. The flask was equipped with liquid and vapor thermometers, and with a reflux condenser and take-off line. Distillate was taken off continuously during heating.

The results of a series of runs made on a 40% UN-8.8% HNO$_3$ solution with various amounts of TBP heated at two different rates are given in Table II. The data show that increasing the heating rate from 0.1 to 1.0°C/min. causes a reaction to occur in mixtures of lower TBP content. Initiation temperature of the spontaneous reaction was found to depend also on the TBP content. The temperature of initiation was found to be in the 140-160°C range (See Figure III). The reaction was typified by a rapid evolution of oxides of nitrogen, foaming, rapid rise in pot temperature, and solidification or drying out of the residue.

The results of the 125 cc-scale tests made on HNO$_3$-TBP systems (no UNH) are given in Table III. The bath temperature was maintained at ~ 180°C during the runs. Distillate was collected continuously at a rate which varied with the size of the charge. Some kind of a self sustained reaction took place in all the tests at ~ 150°C.

Comparison of Runs 2, 3, and 7 indicates the trend toward more vigorous reactions with increasing TBP content at constant boilup. Runs 4 and 5 show a similar tendency. Runs 1 and 2 show that more rapid boilup increases the vigor of the reaction at constant TBP content.

Additional test results are listed in Table IV. Runs 1 and 2 indicate that a very low boilup rate or long refluxing of equal weight HNO$_3$-TBP systems reduces the reaction rate so that it is not detectable. Run 3 gave a rapid reaction at ~ 160°C between TBP and UNH crystals in a 0.21 TBP/UN weight ratio. Run 4 shows that a reaction between TBP and UN-HNO$_3$ occurs at ~ 160°C with a noticeable temperature increase. Run 5 again shows that Amsco is not a factor in the reaction since it distilled off at ~ 110°C, and no reaction occurred with the remaining UN-HNO$_3$ when heated to 186°C. Runs 6 and 7 show no detectable exothermic reaction between TBP and NaNO$_3$ or NaOH respectively up to ~ 175°C.

Experiments in Test Bomb

The intent in carrying out the reaction study in a closed bomb was to permit elevating the temperature to the point where reaction is thermally initiated without change in the concentration of the reactants through distillation of water or water and nitric acid. This objective could be accomplished only in the closed system.

Equipment

The 1 liter test bomb was constructed of 4-inch diameter schedule 80 X stainless steel pipe with a 1-1/2-inch flanged cover plate (Figure II). The cover plate was fitted with 2 thermocouple wells, one for recording the vapor phase temperatures and the second extending to the bottom of the bomb for measurement of liquid phase temperatures. There were 2 pressure lines, one to a Bourdon type gage and the other to a piezo gage recording through an oscilloscope. In addition, a 1/8-inch I. D. distillate take-off line with a condenser was provided. The latter was equipped with a tee to allow pressure to be bled from the bomb without going through the distillate receivers. Finally, two terminals were located in the cover plate with a platinum wire between them to permit attempting periodic external thermal ignition of the vapor phase by a hot wire (electrically heated).

The bomb rested on a sand bath contained in a carbon steel shell. The shell was wrapped with resistance wire for heating, and was encased in magnesia insulation. A thermocouple well was provided in the shell just below the bottom of the bomb. Reaction pressures and their rate of development were measured by a piezo gage-oscillograph unit. The experimental procedure followed with this bomb is described in the Appendix.

The relative volumes of the bomb and the test charges duplicated the relative volumes pertaining to the evaporator incident.

UN-HNO$_3$-TBP SYSTEM

Spontaneous Reaction

Uranyl nitrate solutions containing nitric acid reacted spontaneously with TBP at elevated temperatures. The reaction, once initiated, was highly exothermic and, if the system was closed or restricted, gave rapid rise to high pressures. If the system was not closed or restricted, the observed effect was considerably less violent.

No attempt was made to analyze the organic or inorganic product of the reaction. However, the odor of the reaction residues indicated that some butyric acid was obtained. In two cases with dilute solutions (Table V, Runs 2 and 3) where the reactants were heated to high temperature (150-190°C) but below the spontaneous reaction temperature (195°C) and then allowed to cool to room temperature, no reaction was observed on subsequent heating above the usual initiation temperature. In both cases, the odor of an ester, possibly butyl butyrate, was detected in the reaction mixture.

Initiation Temperatures

When 245 grams (150 cc) of a uranyl nitrate solution, containing 47% by weight of uranyl nitrate and 1.6% nitric acid, was heated with 24.4 grams (25 cc) of tributyl phosphate in the test bomb, a spontaneous reaction was initiated at 195°C. In subsequent experiments, predetermined quantities of water were allowed to distill off, the bomb was closed, and heating continued until reaction was initiated. The temperature of initiation was found to decrease with increase in the concentration of UN, and reached a minimum temperature of approximately 130°C, at which point the liquid temperature required for distillation was the same as the reaction initiation temperature (Figure IV). The approximate calculated concentration of UN at this point was about that of uranyl nitrate tetrahydrate (84.3% UN).

In a similar manner, the effect on the initiation temperature of varying the concentration of TBP relative to UN was studied, using approximately constant UN concentration in the aqueous phase. The runs were made by varying the quantity of TBP added to a standard charge (150 cc) of aqueous uranyl nitrate (38.5% UN-4% HNO_3-Sp.Gr. 1.49) and removing the same amount of aqueous distillate to a calculated uranyl nitrate concentration of about 83-84% by weight in the aqueous phase. The variation of the initiation temperature with the concentration of TBP was found to be minor compared with the effect of UN concentration and remained in the 140 ± 10°C range (Figure V).

Pressure Developed

The pressure (ΔP) increased with increasing quantities of TBP, when the quantity and concentration of uranyl nitrate and nitric acid were held approximately constant, as shown in Figure VI. When the ratio of TBP/UN was held constant, the pressure change increased with increasing concentration of UN in the aqueous phase (Figure VII). It should be noted that the pressure rise is fairly low until an aqueous concentration approaching uranyl nitrate hexahydrate (78.5 wt.%) is attained. At this concentration, the pressure rise is much higher, but may not increase significantly above this concentration. For the purpose of comparison, the observed autogenous pressure in the bomb at the temperature required to initiate the exothermic oxidation reaction is shown in dotted lines in Figure VII.

Since the above ΔP Valves were obtained starting from initial pressures greater than atmospheric and in order to correlate the data with atmospheric runs, it is interesting to determine the pressure which would be obtained from these systems if the reaction could be initiated at atmospheric pressure. For example, with an observed ΔP of 1300 psig starting from 50 psig autogenous pressure (Run 7), the estimated effect at atmospheric pressure (absolute) would be 15/65 of the experimental values of approximately 300 psig. This relation was

checked in a single run (Run 32) where concentration of the
aqueous phase, by distillation, was carried to the point
where the liquid temperature initiated reaction in the open
system (135°C). The observed ΔP was 250 psig and the maximum
rate was 264 psi/sec.

HNO$_3$-TBP System

Only a few closed bomb tests were made on HNO$_3$-TBP mix-
tures (Runs 26-31, Table V).

A violent reaction under an autogenous pressure of
~500 psig was observed starting at ~ 160°C for a TBP/HNO$_3$
ratio of 0.43 (Run 31). A pressure increase of 4600 psi and
a rate of 250,000 psi/sec. were observed.

General Discussion

The experimental data have shown that a vigorous reaction
occurs between TBP and UN and/or HNO$_3$ at temperatures greater
than 130°C. The severity of the reaction and the pressure
developed were found to be directly affected by the amount
of TBP present and the rate at which the mixture was brought
to its initiation temperature.

It can be tentatively concluded that UN-HNO$_3$-TBP is
potentially a pressure producing system and reaction can be
initiated if the system is heated above 130°C at atmospheric
pressure. The pressure produced has been found to be a function
of the pressure in the system at the time of reaction and the
amount of TBP present. Thus, at a TBP/UN ratio of 0.06
(estimated to have been the incident charge), a reaction
occurring against a 50 psig back pressure (plugged column
plates) would produce ~ 200 psi in about 0.2 sec. The
impact strength of the evaporator shell has been estimated at
120-150 psi.

The incident then appears to be the result of the follow-
ing series of events:

1. Presence of TBP (~80 lbs.) in the aqueous uranyl
   nitrate solution.

2. Concentration of the solution to greater than 78%
   UN/total aqueous at temperatures greater than 130°C.

3. Buildup of a 50-100 psi back pressure due to partial-
   ly plugged plates.

A comparison of the incident evaporation data and a typ-
ical bomb run shows how a pressure capable of rupturing the
vessel might be explained.

	Bomb*	Evaporator
Size of container	1000cc	1300 gals.
Size of heel	50cc	65 gals.
Ratio of volumes	20:1	20:1
TBP/UN	0.06	0.06 (min.)
Temperature of Initiation, °C.	135	>135
Pressure at time of reaction, psig	~50	50-100 (assumed)
Pressure developed, psi	~210	210-420
Rate of pressure development, psi/sec.	~1200	

* Table V, Run 21

APPENDIX

Description of TNX Evaporator

Evaporator Shell

Diameter - 6 feet

Height - 5 feet

Dished Ends - 1/4-inch stainless steel

Wall Thickness - 3/16-inch stainless steel sheet (welded)

Evaporator Pot

Diameter - 3 feet

Height - 18 inches

Wall Thickness - 3/16-inch stainless steel

Heating Coils - 6 concentric banks of 1-inch schedule 40 stainless steel pipe

Column

Diameter - 2.5 feet

Height - 17.5 feet

Number of Plates - 8

Number Bubble Caps per Plate - 30

Total Condenser -

Wall Thickness - 3/16-inch stainless steel

Total Capacity

Shell and Pot - 1300 gallons

Column - 525 gallons

Description of TNX Evaporator (continued)

Instrumentation Ranges

Pot Temperature 0-150°C

Pot Sp.Gr. 1.01-2.0

Column Pressure Differential - 20 inches H_2O maximum

Steam Feed Weight Rate Control - 2500 lbs/hr. maximum

Reflux and Take-Off Rotameters - 0-5.0 gpm

Column Vapor Temperature - 0-150°C

Cooling Water Outlet Temperature - 0-150°C

Normal Evaporator Operation

Such experimental studies as solvent extraction, head end, and jet testing result in dilution of the uranium solution ($UN-HNO_3-H_2O$). The water of dilution is removed as required by concentration in the evaporator to a specific gravity of 1.55 to 1.65 (Boiling point: about 110°C).

Normal operation of the evaporator consisted of continuous charging at 3.5 gpm by steam jet. Simultaneously, a take-off rate of 3.5 gpm, and a reflux rate of 1.0 gpm was maintained, thereby retaining about 250 gallons in the pot. The concentration was considered complete when the desired sp. gr. of the solution was attained. The heel was then pumped to a concentrate hold tank.

Incident Evaporation

It was necessary to depart from the above procedure in order to prepare a 44% UN, 1.5% HNO_3 (maximum) solution for head end studies. This requirement necessitated reduction of the acid content of the aqueous uranium solution on hand, which, at 44% UN, contained $\sim$ 4% HNO_3.

Three methods were considered to remove the excess HNO_3 (1) neutralization with sodium hydroxide, (2) addition of UO_3, and (3) evaporation. The neutralization with caustic would introduce sodium ions which were undesirable. The addition of UO_3 was the preferred method, but material was not available at the plant site. Therefore, evaporation to the point where sufficient HNO_3 was removed in the overhead appeared to be the only available method.

Three successful acid-removal runs were made, according to the following procedure, prior to the explosion:

1. Pot batch was charged with $\sim$ 500 gallons solution.

2. Steam input was adjusted to $\sim$ 1000 lbs/hr.

3. Total take-off (no reflux) was used.

4. Operation considered complete when pot temperature reached 150°C, or one hour after sp.gr. reached 1.9.

5. Charge was diluted with water, cooled, pumped to concentrate hold tank.

6. Evaporator and column were flushed with water.

The following data pertaining to the feed charged to the evaporator were obtained as indicated:

Volume: 230 gallons (liquid level recorder)

Composition: UN-44%, HNO_3-2.4% (analysis of feed)

Specific Gravity: 1.56 (specific gravity recorder)

TBP Content: 80 lbs. (from phosphorous analysis of residue after incident)

Amsco Content: 10-15 gallons (found in distillate)

The data on the charge conditions at the instant of the explosion are incomplete because the temperature recorder was not in operation and the specific gravity recorder had gone off scale (greater than 2.0). From the relative volumes and analyses of the distillate and original charge, however, it is inferred that the volume had reached 65 gallons, and the UN concentration was about 80%.

The force of the explosion ripped the evaporator into 6 major pieces, most of the division taking place in the lower half. In the column, the bottom tray was bowed downward more than 1". Other trays were bowed to a lesser extent, some upward, and some downward. Some structural damage to the building was suffered in the immediate vicinity. The sheet metal roofing and siding was extensively dislodged throughout the building.

The bottom column trays were at least partially plugged with a yellowish-green solid. Analysis showed this to be 55% uranium, 0.7% phosphorous.

Outline of Bomb Test Procedure

1. Pipette 150 cc aqueous and 25 cc organic into bomb.

2. Seal bomb, except for takeoff, and heat at 5°C/min.

3. Collect desired amount distillate at 6 cc/min. Measure distillate.

4. Close take-off, thus completely sealing bomb, continue heating.

5. Attempt hot wire ignition every 50 psig pressure increment.

6. Determine pressure at beginning of spontaneous reaction.

7. Continuous temperature record kept by potentiometer-thermocouple unit.

8. Cool bomb, slowly vent off pressure.

9. Open bomb, inspect residue, clean with absorbent paper.

CALCULATIONS

1. Maximum Rate of Temperature Rise in TNX Evaporator:

   Steam Input: 600 #/hour

   Enthalpy: 860 Btu/lbs. (145 psig - 364°F)

   $Q = 600 \times 860 = 516,000$ Btu/hour

   $t = \dfrac{Q}{C_p W + C_{p2}W_2} = 2190°F/hour = 66°C/min.$

2. Maximum Temperature in Pot:

   $U = 100$ Btu/hr. ft.^{2} °F

   $A = 140$ ft.^{2}

   $t = \dfrac{Q}{UA} = 37°F$ $t = 364-37 = 327°F = 164°C$

3. TBP/UN Ratio in Evaporator:

   Residue Analysis: 48.8% U

    0.56% P $\dfrac{TBP}{UN} = 0.06$ (6%)

   Estimated from Organic: TBP = 80#

    UN = 1320# $\dfrac{TBP}{UN} = 0.06$ (6%)

4. Strength of Evaporator Shell:

   Tensile Strength = 60,000 psi

   $P = \dfrac{2tS}{D} = \dfrac{2 \times 3/16 \times 60,000}{5 \times 12}$ 360 psi

   Impact Strength = 20,000 psi

   $P = \dfrac{2tS}{D} = \dfrac{2 \times 3/16 \times 20,000}{5 \times 12}$ 120 psi

COLUMN DETAIL

EVAPORATOR COLUMN

Vent

Water To Hold Tank

Temp. Indicator

Water Wash

Tray Drains

Press. Indicator

Feed Inlet

Jet Discharge

Level Indicator & Sp. Gr.

Temp. Recorder

SEMI-WORKS EVAPORATOR

Cooling Water Out

Water Coils

Press. Indicator

Cooling Water In

Reflux

Trays (Eight)

Bubble Caps

Tray Drains

Spray

Cond. Returns

Steam Inlet

Manhole

Steam Coils

Drain

Liquid

Bubble Cap

Tray

Vapor

Downcomer

Weir

Bubble Cap

FIGURE I

TNX EVAPORATOR

Press. Gage

Preamplifer

To Oscilloscope

Gas Vent

Piezo Gage

Thermocouple Wells

Insulation

Resistance Wire Heater

Sand Bath

Elec. Circuit for Hot Wire

Thermocouple Well

To Condensate Receiver

Scale - 1" = 4"

TEST BOMB

FIGURE II

HEATING RATE AND CONCENTRATION TBP VS. REACTION TEMPERATURE RISE

39.9% UN   8.8% HNO_3 x TBP

25cc aqueous/run
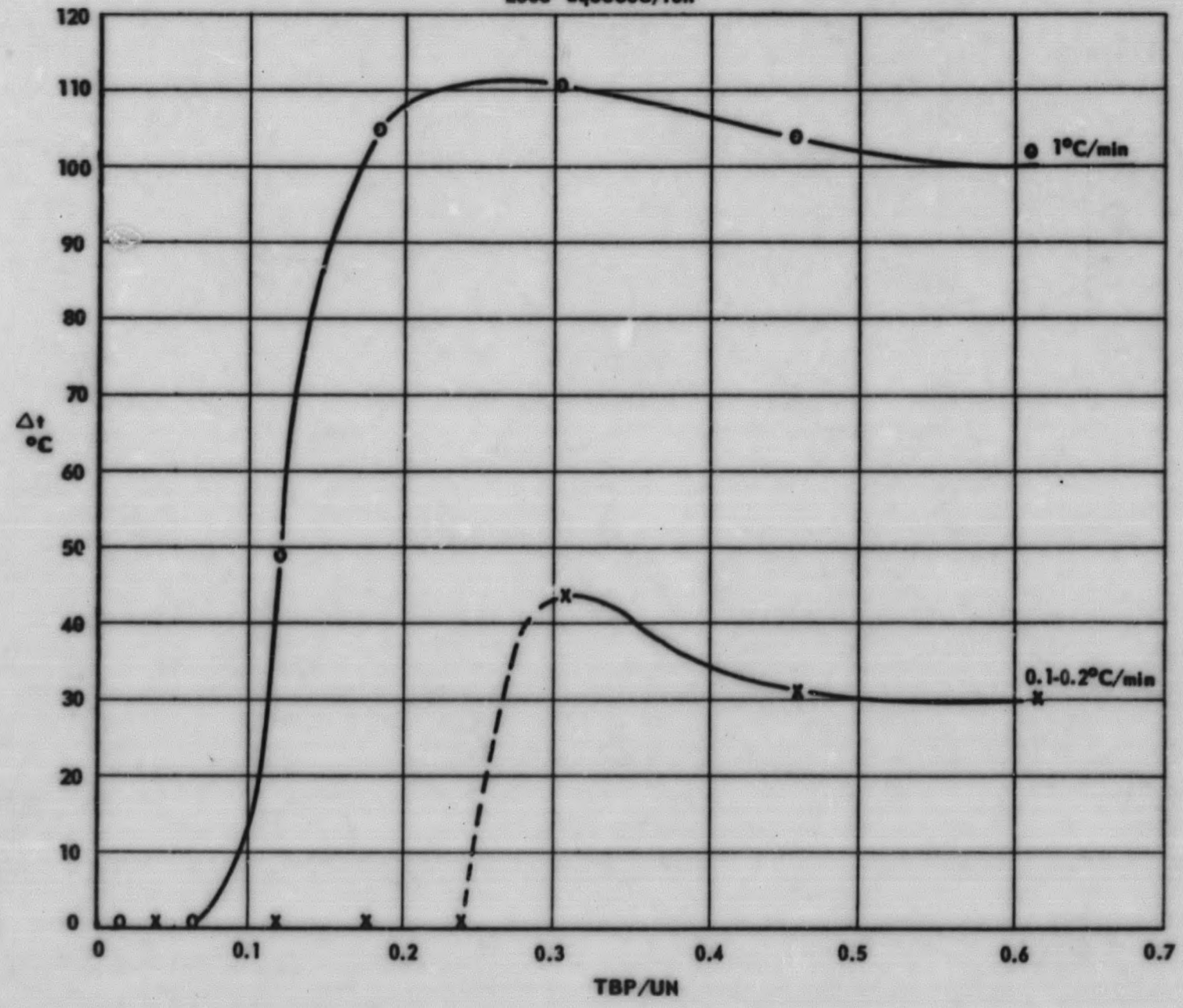
Figure III

EFFECT OF UN CONCENTRATION IN AQUEOUS PHASE ON TEMPERATURE REQUIRED TO INITIATE REACTION
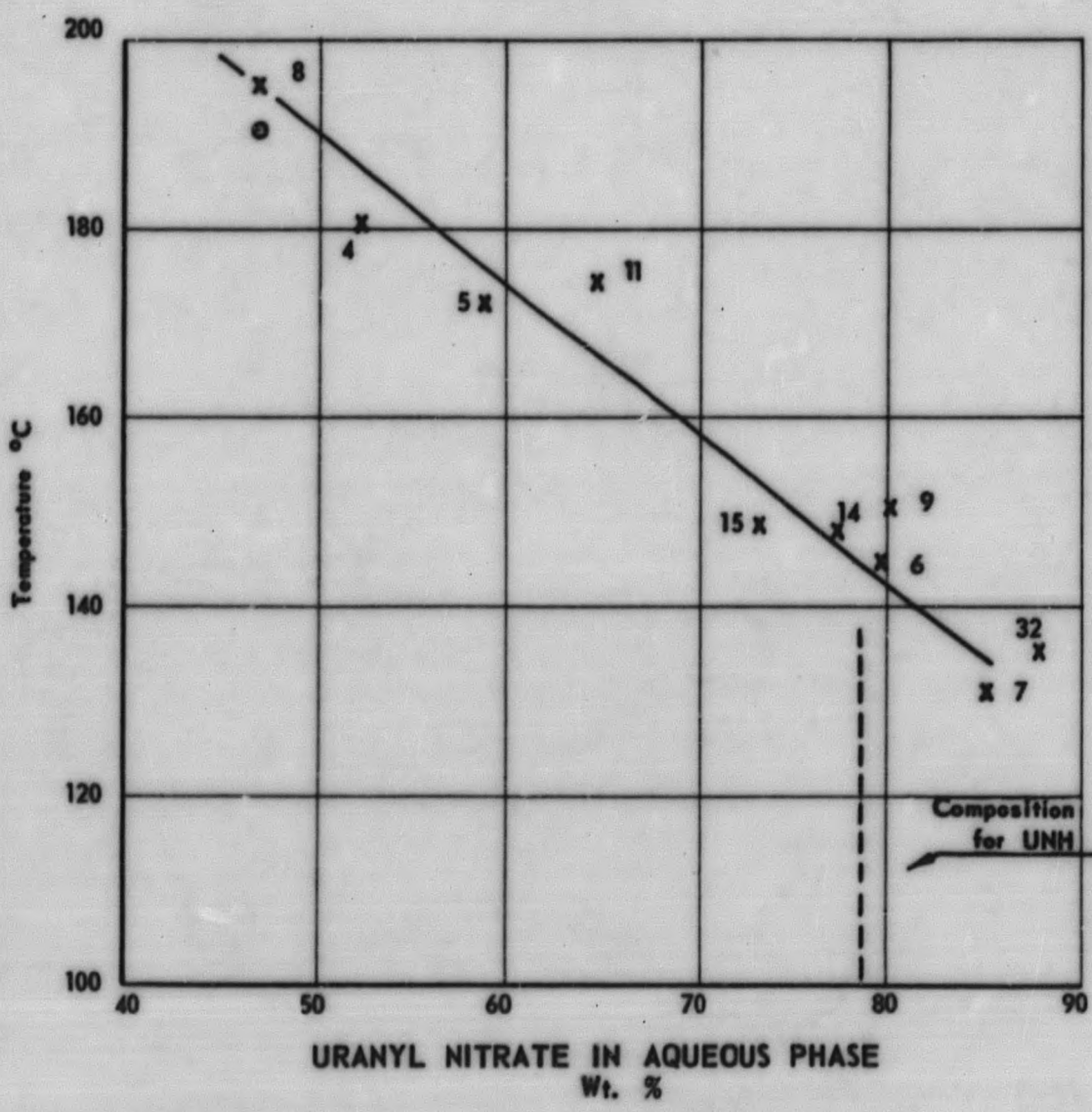
Figure IV

Uranyl Nitrate Solution

    47% Uranyl Nitrate
    1.5% Nitric Acid
    1.635 Sp.Gr.

Charge (Initial)

    150cc Uranyl Nitrate Sol'n
    25cc Tributyl Phosphate

EFFECT OF TBP/UN RATIO ON TEMPERATURE
REQUIRED TO INITIATE REACTION
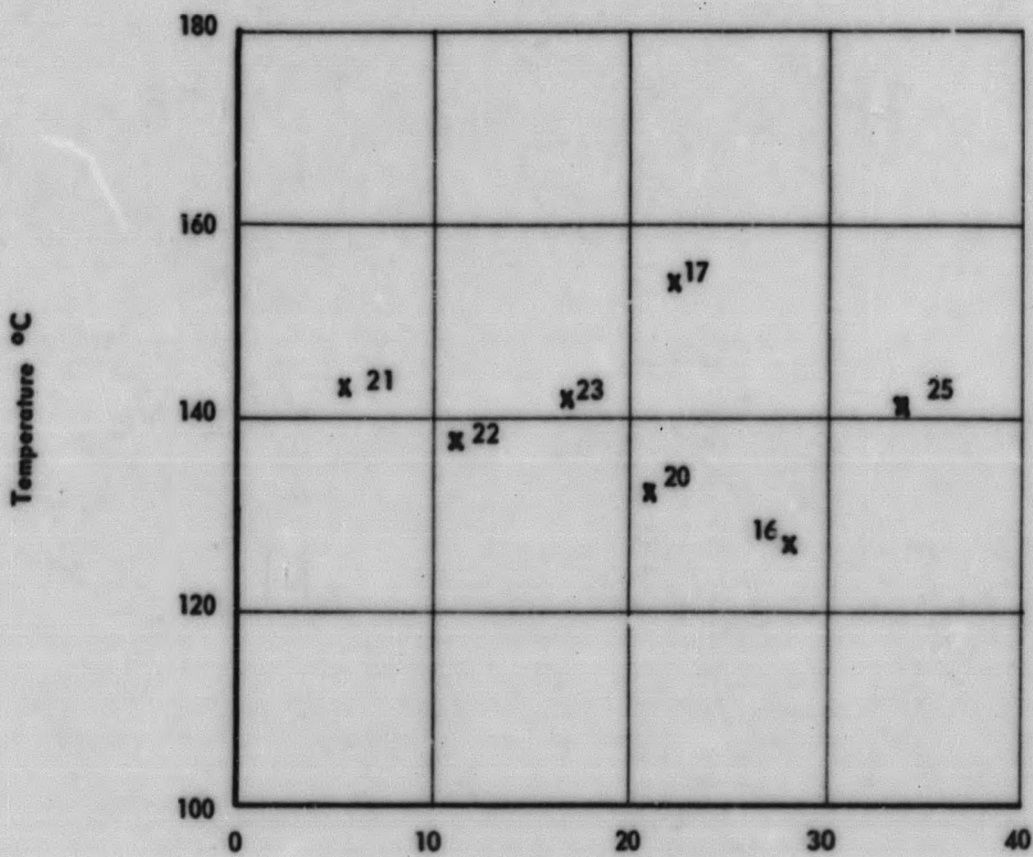
RATIO (TBP/UN) x 100
Conc. of UN in Aqueous Phase Constant
(Approx. 83-84%)

Initial Uranyl Nitrate Sol'n

38.1% Uranyl Nitrate
4% Nitric Acid
1.49 Sp.Gr.

Initial Charge

150cc Uranyl Nitrate Sol'n
5-30cc TBP - Varied

Figure V

EFFECT OF TBP/UN RATIO ON PRESSURE DEVELOPED

Figure VI

RATIO (TBP/UN) x 100
At Constant Conc. of UN in Aqueous Phase
(Approx. 83-84%)
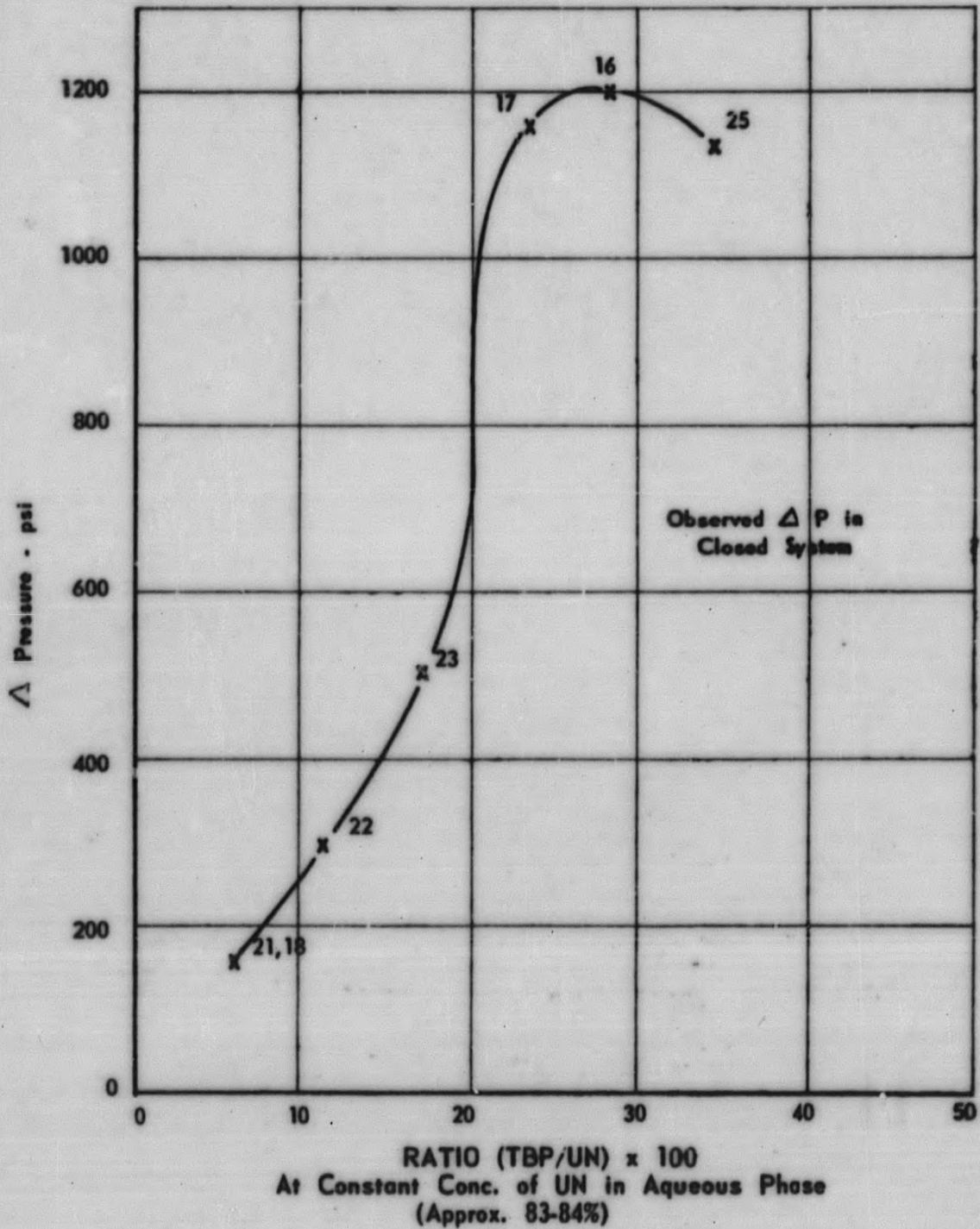
Initial Uranyl Nitrate Sol'n

38.1% UN
 4% HNO_3
1.49 Sp.Gr.

Initial Charge

150cc Uranyl Nitrate Sol'n
5-30cc TBP - Varied

EFFECT OF UN CONCENTRATION IN
AQUEOUS PHASE ON PRESSURE DEVELOPED

URANYL NITRATE IN AQUEOUS PHASE - WT.%

Δ Pressure - psi

Observed P
in Closed System

Observed Autogenous
Pressure at Initiation

Composition of UNH

Initial Uranyl Nitrate Sol'n	Initial Charge
47% Uranyl Nitrate	150cc Uranyl Nitrate Sol'n
1.6% Nitric Acid	25cc Tributyl Phosphate
1.635 Sp.Gr.	
TBP/UN : 0.21	

Figure VII

TABLE I

SUMMARY OF SMALL SCALE TEST RESULTS AT ATMOSHPERIC PRESSURE

Run	System	Liquid Temp. Range, °C	Rapid Reaction	Remarks
1	1 ml organic taken from top of conc. UNH sol'n (W-1: 47% UN 1.6% HNO$_3$)	24-200	none	gummy residue
2	1 ml organic taken from top of conc. UNH sol'n. ≠ 0.1 ml 70% HNO$_3$	24-200	none	gummy residue
3	1 ml aqueous taken from bottom of conc. UNH sol'n. (W-1)	24-200	none	-
4	1 ml TBP-UNH (O)•	24-200	none	gummy residue
5	1 ml TBP-UNH (O)• ≠ 0.1 ml 70% HNO$_3$	24-200	none	gummy residue
6	1 ml TBP-UNH (O)• ≠ 0.1 ml n-Butanol ≠ 0.1 ml 70% HNO$_3$	24-200	none	gummy residue
7	2 ml TBP-UNH (S)• ≠ 0.1 ml 70% HNO$_3$	24-200	none	gummy residue
8	9.5 ml H$_2$O ≠ 0.5 ml n-Butanol ≠ 1 ml 70% HNO$_3$	24-200	none	Butanol distilled off at < 100°C
9	10 ml H$_2$O ≠ 2 ml TBP ≠ 1 ml 70% HNO$_3$	24-200	none	possible slow reaction
10	10 ml UNH (A)• ≠ 2 ml TBP ≠ 2 ml Amsco ≠ 1 ml 70% HNO$_3$	24-200	yes	Amsco distilled off at < 110°C. Reaction initiated at 135°C after Amsco distilled off – Foaming
11	10 ml UNH (A)• ≠ 2 ml TBP-UNH ≠ 0.4 ml 70% HNO$_3$	24-250	yes	Reaction at ∼135°C
12	6.5 ml UNH (A)• ≠ 2 ml TBP-UNH ≠ 1 ml 70% HNO$_3$	24-250	yes	Foaming. Reaction at ∼135°C
13	10 ml aqueous thorium nitrate, 1 ml 70% HNO$_3$, 2 ml TBP	24-250	yes	Foaming. Reaction at ∼140°C

• A - aqueous   S - solid   O - organic

TABLE II

125 cc TESTS AT ATMOSPHERIC PRESSURE
ON UN-HNO₃-TBP SYSTEM

Test Solution: 40% UN 8.8% HNO₃ x TBP
25 cc aqueous charged/run

| Run | STARTING CONDITIONS | | | | INITIATION CONDITIONS | | REACTION | |
	UN gms	HNO₃ gms	TBP gms	TBP/UN	Heating Rate °C/min	Liquid Temp.°C	Temp. Rise °C	Results
1	15.6	3.45	0.58	0.037	0.1 - 0.2	>170	0	No rapid reaction
2	15.6	3.45	1.95	0.125	0.1 - 0.2	>170	0	No rapid reaction
3	15.6	3.45	2.9	0.187	0.1 - 0.2	>170	0	No rapid reaction
4	15.6	3.45	3.9	0.249	0.1 - 0.2	>170	0	No rapid reaction
5	15.6	3.45	4.85	0.311	0.1 - 0.?	144	44	
6	15.6	3.45	7.3	0.467	0.1 - 0.2	138	30	
7	15.6	3.45	9.7	0.62	0.1 - 0.2	140	30	
8	15.6	3.45	0.19	0.012	1.0	>170	0	No rapid reaction
9	15.6	3.45	0.58	0.037	1.0	>170	0	No rapid reaction
10	15.6	3.45	0.97	0.062	1.0	>170	0	No rapid reaction
11	15.6	3.45	1.95	0.125	1.0	138	49	No rapid reaction
12	15.6	3.45	2.9	0.187	1.0	141	123	
13	15.6	3.45	2.9	0.187	1.0	160	87	
14	15.6	3.45	4.85	0.311	1.0	154	91	
15	15.6	3.45	4.85	0.311	1.0	150	131	
16	15.6	3.45	7.3	0.467	1.0	150	104	
17	15.6	3.45	9.7	0.62	1.0	141	102	

TABLE III

ATMOSPHERIC PRESSURE TESTS ON HNO₃-TBP SYSTEMS

Constant HNO₃ Content

Run	STARTING CONDITIONS				INITIATION CONDITIONS				REACTION RESULT	REMARKS
	HNO₃ gms	TBP gms	cc/charge	TBP/HNO₃	Distillate (cc)	Time (min.)	Rate cc/min.	Temp. liquid, °C	Temp. rise, °C	
1	35 (68%)	8.7	34 —	0.36	Refluxed 20.5	4 hrs. 43	0.48	∼155	2	T > T Liquid Bath NO₂ given off
2	35 (68%)	8.7	34 —	0.36	23.5	34	0.69	∼150	180-194	Definite Reaction NO₂ given off
3	35 (68%)	14.2	40 —	0.59	23.5	37	0.63	∼150	180 to 193	Mild Reaction NO₂ given off
4	35 (68%)	24.6	50 —	1.0	20.5	21	0.98	∼150	180 to 206	NO₂ given off
5	35 (68%)	48	73 —	2.0	14	16	0.88	∼150	181 to 210	NO₂ evolved
6	35 (68%)	2.9	28 —	0.12	23	55	0.42	∼150	0	Very slow reaction Copious NO₂ evolved
7	35 (68%)	73	100 —	3.0	12	18	0.67	∼150	180-205	NO₂ evolved

TABLE IV

MISCELLANEOUS 125 cc TESTS AT ATMOSPHERIC PRESSURE

40 cc Charge/run

RUN	STARTING CONDITIONS					INITIATION CONDITIONS		REACTION RESULT	REMARKS
	UN gms	HNO_3 gms	TBP gms	TBP/UN	TBP/HNO_3	Distillate cc/min.	Liquid Temp. °C	Liquid Temp. °C	
1	–	21 (68%)	14.6	–	1.0	Refluxed 48 hours	(120)	–	No reaction NO_2 given off
						13/45	(200)	–	No reaction NO_2 evolved
2	–	21 (68%)	14.6	–	1.0	13.2/150	(200)	–	Possible reaction NO_2 evolved
3	17.5	–	3.6	0.21	–	4.4/21	~160	180 to 280	Large evolution of gas
4	15.6	3.5	5 (DBP)	0.32 (DBP/UN)	1.43 (DBP/HNO_3)	18.1/22	~160	180 to 190	Mild reaction NO_2 given off
5	15.6	3.5	4 (Amsco)	–	–	25.5/42	(186)	–	No reaction. Amsco distilled off below 110°
6	–	5.7 (NaNO3)	14.5	–	2.55 (TBP/NaNO3)	22/17	178	0	No reaction No NO_2
7	–	0.6 (NaOH)	14.5	–	24.2 (TBP/NaOH)	22/20	174	0	No reaction No NO_2

TABLE V

1 LITER BOMB TESTS ON UN-HNO₃-TBP SYSTEMS

Solution B: 46.7% UN 1.58% HNO₃ 1.635 S.G. } ~175 cc charge/run
Solution E: 38.1% UN 4.0% HNO₃ 1.49 S.G.

Run	Sol'n	STARTING CONDITIONS				Distill. Rate gms H₂O min.	INITIATION CONDITIONS Total UN/Aqueous %	T_1 °C	T_v °C	P_i psig	REACTION RESULTS						Run Remarks **
		UN gms	HNO₃ gms	TBP gms	TBP/UN						P_t psig	ΔP g psi	ΔP p psi (max)	dP p/dt psi/sec (max)	ΔT v/Δt °C/sec	ΔT l/Δt °C/sec	
1	B	115	3.9	24	0.21	unknown	unknown	160	132	~75	>300	>300	-	-	44/40	-	Pot contents probably concentrated while bomb sat overnite vented.
2	B	115	3.9	4	0.21	none	47.1	203	175	>300	-	-	-	-	-	-	Possible leakage of reaction gases while bomb sat overnite not vented.
						~120/?	~92	190	153	40	-	-	-	-	-	-	
3	B	115	3.9	24	0.21	none	47.1	190	164	200	-	-	-	-	-	-	Temperature not brought up high enough (see run 8)
						120/?	92	130	130	0	-	-	-	-	-	-	
4	B	115	3.9	24	0.21	25/?	52.5	180	140	»140	~350	>160	150	-	20/25	-	Reaction while hot wire was on.
5	B	115	3.9	24	0.21	50/8	59/5	172	148	>150	~320	>150	130	-	30/20	-	-
6	B	115	3.9	24	0.21	100/20	80.0	144	127	75	~750	>225	>260	-	80/20	-	Reaction while hot wire was on; pressure rising 1 psi/sec at reaction.
7	B	115	3.9	24	0.21	110/21	85.8	130	110	50	«1350	»300	1300	1020	>190/15	-	Pressure using 2 psi/sec at reaction.
8	B	115	3.9	24	0.21	none	47.1	195	166	>300	>300	-	-	-	8/35	-	-
9	B	115	3.9	24	0.21	102/16	81.0	150	116	~50	«1300	»300	1280	5040	180/15	-	-
10	HNO₃	-	4.7	24	-	125/19		188	168	300	-	-	-	-	-	-	-
11	B	115	3.9	24	0.21	67/13	65.0	174	152	160	~335	>140	175	-	40/25	28/25	-
12	B	7.5	4.4	24	3.2	125/20	16.5	186	168	>300	-	-	-	-	-	-	Found leak at 180 psig
13	B	115	3.9	5	0.043	95/35	77.0	150	129	140	190	50	-	-	16/35	20/35	Stood overnite sealed after 95cc distillate removed, NO₂ present at end.
14	B	115	3.9	24	0.21	97/17	78.3	148	128	90	690	600	540	250	80/20	75/20	Temperature record very similar to Run 6.
15	B	115	3.9	24	0.21	87/16	73.3	152	138	150	520	370	260	-	50/15	40/15	-
16	E	85	9.0	24	0.28	120/18	85.5	127	118	90	»1000	«1200	-	-	>180/20	>170/20	-

TABLE V (CON'T.)

Run	Sol'n	UN gms	HNO₃ gms	TBP gms	TBP/UN	Distill. Rate gms H₂O/min.	Total UN/Aqueous %	T_l °C	T_v °C	P_i psig	P_t psig	ΔP_g psig	ΔP_p psi (max)	dP_p/dt psi/sec (max)	ΔT_v/Δt °C/sec	ΔT_l/Δt °C/sec	Run Remarks **
17	E	85	9.0	19.5	0.227	124/21	86.0	154	130	70	~1230	>1000	1160	790	110/23	130/23	Bomb charged, sealed, stood overnite, 90 psig at start (R.T.), distilled 124 cc at 75 psig.
18	E	85	9.0	5	0.058	120/75	83.5	133	95	30	190	160	85	—	60/20	50/20	Heating mantle trouble at 90 cc distillate, took 35 min. to repair, NO₂ present at end.
19	E	85	9.0	—	—	120/25	83.5	176	165	150	—	—	—	—	—	—	NO₂ present at end.
20	E	115	12.0	24	0.21	161/22	84.0	132	114	50	~1500	~1450	1060	944	>186/10	>168/10	—
21	E	85	9.0	5	0.058	117/26	81.1	143	120	50	210	160	126	125	72/15	48/15	NO₂ present at end
22	E	85	9.0	9.7	0.113	119/18	82.6	138	114	50	350	300	183	95	70/20	67/40	—
23	E	85	9.0	14.5	0.169	115/30	79.7	142	123	70	570	500	336	361	127/20	86/37	—
24	E	85	9.0	29.1	0.339	50/16	47.0	140	—			—	—	—		73/30	NO₂ present at end
25	E	85	9.0	29.1	0.339	113/21	78.3	141	117	70	1070	>1000	1140	543	>180/15	>100/15	—
26	HNO₃–TBP in pot	Trace (68%)	105	30	—	none	—	260	150	~ 500	>1500	>1000	>1600	—	>150/1	>140/1	—
27	HNO₃–TBP in pot	Trace (68%)	53	15	—	none	—	161	150	~ 350	fittings found leaking			No reaction			Fittings leaked at 350 psig.
28	HNO₃–TBP Pot Clean (68%)		80	22	—	none	—	158	140	~ 500	>1500	>1000	>2200	18500			Gasket blown, NO₂ present.
29	HNO₃–TBP Pot Clean (68%)		27	7.5	—	none	—	156	156	~160	fitting leaking, very little charge left						Fitting leaking, temperature falling off, very little liquid left in pot, NO₂.
30	HNO₃–TBP Pot Clean (68%)		53	15	—	none	—	180	164	420	no reaction, temps. falling off						Temperature falling off after max. reached. Very little liquid left in pot.
31	HNO₃–TBP Pot Clean (68%)		75	22	—	none	—	~160	~150	> 200	>1200	>1000	4600	250000	>150/1	>140/1	—
32	E	115	12.0	24	0.21	167/34	87.7	135	122	0	250	250	190	264	57/25	75/25	—

* Based on distillate
** Hot wire ignitions (vapor) attempted every 50 psi rise

t_l = liquid temp.
t_v = vapor temp.
P_i = pressure at initiation
P_t = total pressure
ΔP_g = rise in pressure by Bourdon gage
ΔP_p = rise in pressure by Piezo gage
$\Delta T_l/\Delta t$ = rate of liquid temp. rise (°/sec)

dP_p/dt = rate of pressure
$\Delta T_v/\Delta t$ = rate of vapor temp. rise (°/sec)

END