BEHAVIOR OF TRIBUTYL PHOSPHATE IN A-LINE PROCESSES

by

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ABSTRACT

The chemical and physical properties of uranyl nitrate-tributyl phosphate adduct $(\text{UO}_2)(\text{NO}_3)_2(\text{TBP})_2$ were studied to define optimum, safe operating conditions for denitration of uranyl nitrate (UN) solutions containing low concentrations of adduct.

The distribution of TBP between aqueous UN solutions and organic phases (TBP pure or diluted in n-paraffin) was measured.

Specific gravity measurements confirmed published data for aqueous UN solutions, but disagreed with literature data for 100% TBP. Intersection of the UN specific gravity curve and the 100% TBP data of this work indicated that phase inversion cannot occur when the aqueous phase contains ≥ 330 g U/l.

Thermal decomposition of adduct occurs in one gradual weight loss step below 170°C and in two successive steps above 170°C . Rate constants for the first reaction were calculated for 130 to 210°C . The major flammable decomposition product was 1-butene; inorganic gases formed were N_2 , NO, N_2O , CO, and CO_2 .

Adduct decomposition during denitration of UN was characterized by foaming and by gas evolution (mostly nonflammable) at 135 to 185°C .

Maximum flammable gas evolution and potential self-heating by TBP oxidation were calculated.

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BEHAVIOR OF TRIBUTYL PHOSPHATE IN A-LINE PROCESSES

INTRODUCTION

On February 12, 1975, an uncontrolled, exothermic reaction occurred in the Savannah River Plant (SRP) facility for UO_3 production. This facility (A-Line) receives dilute uranyl nitrate (UN) solution (~ 90 g U/l) from the Purex solvent extraction process, concentrates the solution by two evaporation steps, and converts the concentrated solution (~ 1200 g U/l) to UO_3 by thermal denitration. The excessive reaction occurred when >30 gal of tributyl phosphate (TBP) in the form of $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ (adduct) was accidentally charged to a denitrator; the adduct decomposed forming flammable gases which escaped into the denitrator room and subsequently ignited.

Small amounts of entrained or dissolved TBP enter A-Line process streams, and all of the TBP cannot be removed from the uranyl nitrate solutions with present equipment. Thus, the denitrators must be operated to slowly decompose small amounts of TBP under controlled conditions. To define the optimum denitrator conditions, thermal decomposition of adduct, denitration of uranyl nitrate with adduct present, and gas evolution during adduct decomposition were studied; some physical properties of the TBP-uranyl nitrate system were also determined. In addition, maximum flammable gas evolution and potential heat releases during adduct decomposition were calculated.

EXPERIMENTAL

TBP Distribution Measurements

The distribution of TNP into UN solutions was determined by contacting 20 ml of aqueous UN solutions (50 to 400 g U/l) with 2 ml of 100%, 90%, and 30% TBP (n-paraffin diluent). The n-paraffin diluent consists of a mixture of C_{13} - C_{14} hydrocarbons with an average molecular weight of 191. The phases were gently agitated in a shaker bath at the chosen temperature (25 to 65°C) for 23 to 64 hr and were allowed to separate for 16 to 64 hr. This extended procedure was followed in order to: 1) reach equilibrium without vigorous agitation and possible entrainment, and 2) achieve complete phase separation without removing the vials from the constant temperature bath for centrifugation.

TBP concentrations in the UN solutions were determined by both phosphate and infrared (IR) analyses. For the phosphate method, TBP was oxidized to PO_4^{3-} by heating in a $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}_2$ media until SO_3 fumes were observed. The PO_4^{3-} concentration was then determined by a molybdenum blue colorimetric method.¹ For the IR method, a 10-ml aliquot of UN solution containing dissolved TBP was stripped with three ~3-ml volumes of CCl_4 , and the combined CCl_4 strip was diluted to 10 ml in a volumetric flask. The TBP concentration was determined by measuring the absorbance of the CCl_4 solution at 2876 cm^{-1} (C-H band) and by use of a suitable calibration curve. Extreme care was taken in pipetting to avoid contaminating UN samples with undissolved TBP solution, especially with 30% and 90% TBP, because n-paraffin interferes by absorption in the same IR region.

Specific Gravity Measurements

For specific gravity measurements, 100% and 90% TBP (n-paraffin diluent) solutions were contacted twice with aqueous UN solutions at aqueous-to-organic volume ratios of 2.5 at 25°C . Equilibrated aqueous solutions were analyzed for U and HNO_3 , and specific gravities of the organic phases and several aqueous solutions were determined using 5- or 10-ml volumetric flasks. The flasks were calibrated to $\pm 0.002\text{ ml}$ at 25°C with triply distilled water. Volume corrections for 45°C and 65°C were calculated assuming the cubical coefficient of expansion of borosilicate glass to be $0.000025^\circ\text{C}^{-1}$.²

Thermogravimetric-Mass Spectral Analyses

For thermogravimetric-mass spectral analyses (TGA-MS) a modified Model RH electrobalance (Cahn Instrument Co., Paramount, CA) was used with both helium and 80% He - 20% O_2 atmosphere. The evolved gases were fed to a Model MS-10 mass spectrograph (AEI Scientific Apparatus Corp., Elmhurst, IL).

Gas Chromatographic Analyses

Gas chromatographic analyses were made with a Hewlett-Packard Model 5756B gas chromatograph equipped with thermal conductivity and flame ionization detectors, and a Finnigan Model 1015C quadrupole mass spectrometer (QMS) fitted with a glass jet separator for sample enrichment in the gas stream. The helium flow rate was 100 cc/min; approximately 45 cc/min is supplied to each detector, and 10 cc/min is supplied to the QMS.

Inorganic and lower molecular weight organic gases (methane through butane) were separated with a 6-ft glass column. The column was packed with 30/60-mesh 5A molecular sieve which was held at 24°C with dry ice for five minutes and then heated at 40°C/min to 300°C.

The polar organic compounds (organic acids, alcohols, aldehydes, ketones, and nitrates) were separated on a 6-ft glass column packed with 10% *Carbowax**-20M terephthalic acid on 100/120 mesh high-performance Chrom W. The column was heated from 50 to 180°C at 10°C/min.

Oscillographic strip chart recordings of mass spectra were interpreted manually by comparison with standard mass spectral compilations.³ The concentrations of organic acids were too low for definite mass spectral identification. Mass spectral data agreed with reference spectra for all other observed compounds.

Denitration Tests

Denitration experiments (actually a combined hydrate evaporation and denitration) were conducted with 250 ml of initial UN solution (400 g U/l) in 500-ml stainless steel beakers; the beakers were equipped with thermocouples to measure the temperature of the bulk UN solution and the beaker surface. The beakers were insulated with asbestos to facilitate temperature control. In most tests, the heating rate was ~2°C/min during adduct decomposition. Stirring rates were 100 rpm except in tests using SRP feed solutions. For these solutions, the stirring rate was decreased to 18 rpm for better representation of SRP operation.

Materials

$\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ was prepared both by repeated equilibration of TBP with 400 g U/l solutions and by contact of TBP with several fresh quantities of solid uranyl nitrate hexahydrate (UNH) (until released water of hydration was no longer observed, and the maximum specific gravity was obtained). Analyses of adduct samples are shown in Table 1. The analytical results and literature data⁴ indicate that the adduct prepared by contacting aqueous solutions probably contained 0.2 to 0.3 wt % extracted water.

* Registered tradename of Carbide and Carbon Chemical Co.

TABLE 1

Elemental Analyses of Adduct Used in
Thermogravimetric Analyses

Element	Composition, wt %		
	Calculated	Sample A ^a	Sample B ^b
U	25.69	25.19	25.90
P	6.68	6.48	6.61

a. Prepared by repeatedly contacting aqueous 400 g U/l solution with TBP.

b. Prepared by contacting solid UNH and TBP.

TBP, n-paraffin, and Antifoam B emulsion (Dow-Corning) were obtained from the Savannah River Plant. All other chemicals used were reagent grade.

TBP DISTRIBUTION STUDIES

The equilibrium TBP content of UN solutions was measured to determine the maximum quantity of TBP which could enter A-Line process streams by this mechanism. The solubility or distribution* of TBP in UN solutions decreased as uranium concentration increased (Figures 1 and 2). Thus, part of the TBP dissolved in the dilute UN solution (90 to 100 g U/l) from solvent extraction will slowly separate as a second adduct phase after the UN solution is concentrated to ~400 g U/l in A-Line.

TBP concentration decreases with increasing n-paraffin diluent concentration (Figure 2), particularly at <200 g U/l, because TBP has a lower activity in the dilute phase and, therefore, is at equilibrium with a lower concentration of aqueous TBP. A similar effect of diluent concentration was observed in ORNL studies.⁵

Results of the IR method of analysis were consistently higher than those of the phosphate method (Figures 1 and 2). To investigate this difference, TBP distribution into water was measured by both methods and compared in Table 2 to results from an independent method⁵ (³²P counting). Because the ³²P results are about midway between the phosphate and IR results, this comparison gives no basis for determining which method is more accurate. However, the

*The term "solubility" applies only for 100% TBP; with excess TBP or with diluent present, TBP is distributed between the organic and aqueous phase at equilibrium.

fair agreement between all three methods indicates that the phosphate and IR methods are accurate within a factor of 2. For A-Line process applications, the IR results are most pertinent because a similar method is used by SRP laboratories to analyze A-Line solutions.

FIGURE 1. Distribution of TBP (in n-paraffin) into Aqueous Uranyl Nitrate Solutions at 25°C (Analyzed by Phosphate Method)

FIGURE 2. Distribution of TBP (in n-paraffin) into Aqueous Uranyl Nitrate Solutions at 25°C (Analyzed by Infrared Method)

TABLE 2

Distribution of TBP in Water at 25°C

TBP, vol % ^a	TBP Concentration, mg/l		
	Method ^b	IR Method ^b	³² P Method
30	198	305	235 ^c
90	314	420	390 ^c
100	336	466	410

- a. Diluent is n-paraffin in present work; ORNL used Amsco 123-15, a similar kerosene-type diluent.
- b. Phosphate results are the average of three determinations; the IR results are one measurement.
- c. Obtained by graphical interpolation of ORNL data in Reference 5.

The effect of temperature on TBP distribution could not be interpreted with certainty because of irregularities in the data. The difference between the IR results and the phosphate results increased with increasing temperature and TBP concentration. This relationship suggested a chemical effect rather than analytical difficulties. In addition, as the temperature was increased from 25 to 45°C, TBP distribution decreased, especially at lower uranium concentrations (Figure 3). A decrease in TBP distribution was also observed by Kennedy and Grimley⁶ for 16 to 22°C. However, the 55 and 65°C experiments of the present work exhibited a reverse in this trend with the 65°C data (confirmed by duplicate runs) showing the highest results of any experiment in the 200 to 400 g U/l range. This unexpected temperature effect also suggested some chemical phenomenon.

Investigation indicated that TBP hydrolysis was the cause of these irregularities. Some distribution experiments lasted ~80 hr before the samples were analyzed. TBP hydrolysis was calculated using published rate constants⁷ for TBP in 0.25M UN-0.05M HNO₃ indicated 0.08% hydrolysis occurred after 80 hr at 25°C and 7.7% hydrolysis after 80 hr at 65°C. Thus, enough hydrolysis could have occurred at the higher temperatures to affect the distribution measurements. However, measurement of TBP distribution at 25°C following equilibration times of 6 to 64 hours showed that any change in aqueous TBP concentration due to hydrolysis was less than experimental error.

FIGURE 3. Distribution of TBP into Aqueous Uranyl Nitrate Solutions as a Function of Temperature. Data at 35 and 55°C were not shown because of overlap. (Analyzed by Phosphate Method)

SPECIFIC GRAVITY OF TBP AND URANYL NITRATE SOLUTIONS

Specific gravity data for UN solutions and for TBP in equilibrium with UN solutions are important to A-Line operations to allow choice of operating conditions which will prevent phase inversions (heavy organic layer), and to design a coalescer unit for possible use in removing entrained organic material.

The results obtained agree well with literature data⁴ (Figure 4) except for 100% TBP. The steep slope of the literature data⁴ is based on one high result at 500 g U/l in the aqueous phase. In the present work, repeated contact of TBP with fresh quantities of crystalline UNH yielded a maximum specific gravity of 1.467. The high literature value is therefore questionable. Intersection of the UN specific gravity curve and the 100% TBP data of the present work indicated that phase inversion cannot occur when the aqueous phase contains ≥ 330 g U/l.

FIGURE 4. Specific Gravity of TBP and Uranyl Nitrate Solutions

The effect of temperature on specific gravity of UN and TBP solutions was also determined. Specific gravities of UN solutions (Table 3) decreased only a few percent as the temperature increased from 25 to 65°C. Similar decreases were observed for TBP solutions in equilibrium with UN solutions (Table 4). TBP specific gravity decreased due to less uranium extraction at higher temperatures and thermal expansion effects. The effect of thermal expansion alone is shown in Table 5; in this case, specific gravity of the TBP solution in equilibrium with 373 g U/l was measured at 25, 45, and 65°C without additional equilibration with the aqueous phase. Based on the observed changes between data in Table 5 and data in Table 4, thermal expansion was the major cause of the observed specific gravity changes. Because specific gravity of TBP and UN solutions decreased with increasing temperature by approximately the same percent, operating conditions that prevent phase inversion at 25°C will also apply at higher temperatures.

TABLE 3

Effect of Temperature on the Specific Gravity
of Uranyl Nitrate Solutions

<i>U Concentration, g/l</i>	<i>Temperature, °C</i>	<i>UN Specific Gravity</i>	<i>Specific Gravity Difference from 25°C, %</i>
48.9	25	1.066	-
	45	1.059	-0.66
	65	1.048	-1.69
197.5	25	1.267	-
	45	1.257	-0.79
	65	1.247	-1.58
387.6	25	1.536	-
	45	1.521	-0.98
	65	1.506	-1.95

TABLE 4

Effect of Temperature on the Specific Gravity of TBP Contacted with Uranyl Nitrate Solutions

<i>TBP Concentration, vol %</i>	<i>Original Aqueous U, g/l</i>	<i>Equilibrium Aqueous U, g/l^a</i>	<i>Temperature, °C</i>	<i>TBP Specific Gravity</i>	<i>Specific Gravity Difference from 25°C, %</i>
100	350	340.0	25	1.441	-
		322.0	45	1.431	-0.69
		332.6	65	1.404	-2.57
100	400	382.0	25	1.441	-
		379.4	45	1.433	-0.56
		382.3	65	1.408	-2.29
90	350	329.5	25	1.379	-
		337.9	45	1.357	-1.60
		339.8	65	1.346	-2.39
90	400	379.1	25	1.382	-
		380.2	45	1.364	-1.30
		388.0	65	1.352	-2.17

- a. Decreased uranium extraction at higher temperatures should be reflected by increasing equilibrium aqueous uranium concentrations. This effect is not observed for the 100% TBP data probably because of variations in the uranium concentration of the nominal 350 g U/l and 400 g U/l solutions.

TABLE 5

Effect of Thermal Expansion on the Specific Gravity
of TBP Equilibrated with Uranyl Nitrate Solution

<i>Temperature, °C^a</i>	<i>Specific Gravity</i>	<i>Specific Gravity Difference from 25°C, %</i>
25	1.446	-
45	1.427	-1.31
65	1.410	-2.49

- a.* Equilibrium uranium concentration was 373 g U/l at 25°C. The TBP solution was heated to 45°C and 65°C for specific gravity measurements without additional equilibration with the aqueous uranyl nitrate solution.

THERMAL DECOMPOSITION OF ADDUCT

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) of adduct showed weight loss in two successive reactions at $\geq 170^\circ\text{C}$, and only a single gradual weight loss at lower temperatures (Figure 5). The weight loss at lower temperatures and the weight loss from the first reaction at $\geq 170^\circ\text{C}$ correspond closely to the formation of anhydrous UN and phosphoric acid. (The presence of entrained water or the decomposition of organic molecules could provide the hydrogen needed to form phosphoric acid.)

Weight loss calculations for the second reaction suggest formation of one or more of the following combinations of products (in order of decreasing agreement with experimental results):

- Uranyl phosphate and pyrophosphoric acid
- Uranyl phosphate and phosphoric acid
- UO_3 and pyrophosphoric acid
- UO_3 and phosphoric acid

FIGURE 5. Thermogravimetric Analysis of Adduct

In some cases, the second reaction of adduct appeared to follow zero-order kinetics during part of the reaction. Because denitration of uranyl nitrate follows zero-order kinetics⁸ and weight loss calculations indicated UO_3 formation, the second adduct reaction was thought to involve denitration of UN. However, TGAs of UNH did not resemble adduct TGA curves during the second adduct reaction. Also, mass spectral analyses of evolved gases showed that organic products are formed during both the first and second adduct reactions. Denitration of UN may be occurring during the second adduct reaction, but other reactions are occurring simultaneously.

Residues were obtained from heating of adduct to 130, 170, and 210°C; these residues were examined to determine the reactions occurring on heating adduct. Chemical analyses indicated that the residues contained mostly uranium and phosphate. As expected, the quantity of residual organic material decreased with increasing temperature. X-ray diffraction analyses showed some evidence of $\text{U}_3(\text{PO}_4)_4$ and UP_2O_7 in the 130°C residue; the 170°C and 210°C residues were amorphous and could not be identified. Products in the residues may not be the products of the primary adduct decomposition reaction because of additional reactions occurring within the residue.

Rate Constant Calculations for First Adduct Reaction

The weight loss (weight of volatile reaction products evolved) of adduct samples with time were measured to determine decomposition rate constants for the first adduct reaction.* The weight of adduct at any intermediate time during the first reaction minus the final weight at the completion of that reaction represents the weight of volatile component (decomposition products) remaining in the sample. The quantity was assumed to be proportional to the amount of adduct not decomposed. A similar approach was used by Nichols⁹ in a previous study, in which the volume of gas released was assumed to be proportional to the extent of reaction. The data followed first-order kinetics as shown in Equation 1

$$\log C_t = \left(\frac{-k_1}{2.303} \right) t + \log C_0 \quad (1)$$

where C_t is the concentration of adduct at time t , k_1 is the first-order rate constant, t is the time, and C_0 is the initial concentration of adduct. Plots of $\log$ (weight of volatile component) versus time were linear (Figure 6), and rate constants were calculated by least-squares calculations of the slopes of these linear plots. The rate constant results are compared to those of Nichols' work⁹ with $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-TBP}$ adduct in Figure 7.

The variation of rate constants with temperature can be represented by the Arrhenius equation (Equation 2)

$$\log_{10} k = \left(\frac{-E_a}{2.303R} \right) \frac{1}{T} + C \quad (2)$$

where k is the rate constant, E_a is the activation energy, R is the gas constant ($1.99 \text{ cal/mole}^\circ\text{K}$), T is the absolute temperature, and C is a constant of integration. Least-squares calculations of the slope and y-intercept of the Arrhenius equation were made using the rate constants measured in helium, those measured in simulated air, and the combined data. The results are compared to Arrhenius parameters for previously reported rate constants⁹ in Table 6. The helium atmosphere data and the simulated air data are significantly different, but reasons for faster adduct decomposition in helium than in simulated air (if a real effect) are not known. Thus, Arrhenius parameters for the combined data were used to calculate rate constants for denitrator safety calculations presented in later sections of this report.

* The second adduct reaction did not follow simple kinetics. Because the first adduct decomposition step was the fastest reaction, rate constants based on the first reaction will be used in safety calculations presented later.

FIGURE 6. First Reaction in Thermal Decomposition of Adduct

FIGURE 7. Adduct Decomposition Rate Constants as Function of Temperature

TABLE 6

Least-Squares Fit of Arrhenius Equation to Adduct Decomposition Rate Constants

<i>Basis</i>	<i>Slope</i>	<i>Intercept</i>	<i>E_a</i> , <i>kcal/mole</i>
Present helium data	-6603	14.85	30.3
Present 80% helium - 20% oxygen data	-5158	11.59	23.6
Present combined helium and 80% helium - 20% oxygen data	-5704	12.81	26.1
Reference 9 ^a	-6070	13.96	27.8

a. For TBP equilibrated with 1.5M UN - 3.0M HNO₃.

Analysis of Gaseous Decomposition Products

Samples of pure adduct and organic material (>95% adduct) from A-Line tanks were thermally decomposed in air under non-isothermal conditions. Evolved gases were collected by water displacement and were analyzed by gas chromatography (GC). The results (Table 7) indicated that the major flammable product was butene or butyne, but positive identification by GC alone was not possible. Analyses of the gases with an MS-10 mass spectrometer also suggested unsaturated C₄ compounds; these analyses could not be confirmed because the observed spectra were a composite of parent peaks and fragmentation patterns of all the gaseous products (Table 8).

The butyl compound was identified by interfacing a quadrupole mass spectrometer (QMS) with the gas chromatograph to allow analysis of each gas as it exited the column. The organic gases (Table 9) were identified by their fragmentation pattern and by comparison to standard mass spectral compilations.³ The major flammable component was identified as 1-butene. Both 1-butene and trans-2-butene were suggested by the butene mass spectra, but mass peak ratios suggest 1-butene is a better choice. Concentrations of other organic compounds indicated by MS-10 mass spectral analyses (Table 8) were too low for detection by the GC-QMS technique.

TABLE 7

Analysis of Gases Evolved by Thermal Decomposition of Adduct

Gas	<u>Concentration of Gas Evolved, vol %^a</u>		
	<u>A-Line</u> Adduct	Duplicate Samples of Pure Adduct	
O ₂	0.06	0.07	0.05
N ₂	21.5	24.9	19.2
NO	32.1	28.2	14.1
N ₂ O	8.9	11.7	9.3
CO	4.9	9.3	5.4
CO ₂	17.8	21.7	15.8
1-Butene	17.8 (20)	20.9 (11)	40.0 (24)
Other Hydro- carbons	<u>0.2</u>	<u>0.4</u>	<u>0.4</u>
Total	103.3	117.2	104.3

^a. All results except those in parentheses were obtained with a 5A Molecular Sieve column. The latter values for butene (obtained with a 10% *Carbowax* 20M - terephthalic acid column) are more reliable.

TABLE 8

Gaseous Adduct Decomposition Products Indicated by Thermogravimetric-Mass Spectral Analyses

<i>Compound^a</i>	<i>Mass/Charge (Ionic Species)^b</i>
H ₂ O	18(P), 16(O)
CO ^c	28(P), 16(O)
N ₂ ^c	28(P), 14(N)
C ₂ H ₄	28(P), 27(C ₂ H ₃), 14(CH ₂)
NO ^c	30(P), 16(O), 14(N)
O ₂ ^c	32(P), 16(O)
C ₂ H ₆	30(P), 15(CH ₃)
N ₂ O ^c	44(P), 28(N ₂), 16(O)
CO ₂ ^c	44(P), 28(CO), 16(O)
NO ₂	46(P), 30(NO), 16(O), 14(N)
C ₄ H ₆ (butyne)	54(P), 41(C ₃ H ₅), 40(C ₃ H ₄), 39(C ₃ H ₃), 38(C ₃ H ₂), 27(C ₂ H ₃), 15(CH ₃), 14(CH ₂)
C ₄ H ₈ ^c (butene)	56(P), 41(C ₃ H ₅), 40(C ₃ H ₄), 29(C ₂ H ₅), 27(C ₂ H ₃), 15(CH ₃), 14(CH ₂)
C ₄ H ₁₀ (butane)	58(P), 44(C ₃ H ₈), 29(C ₂ H ₅), 15(CH ₃) 14(CH ₂)
C ₄ H ₁₀ O (butanol)	74(P), 56(P-H ₂ O), 41(P-H ₂ O and CH ₃), 28(P-H ₂ O and C ₂ H ₄), 18(H ₂ O), 15(CH ₃), 14(CH ₂)
C ₄ H ₈ O ₂ (butyric acid)	P not observed, ^d 71(P-OH), 60(CH ₃ COOH) ^d , 45(COOH), 43(C ₃ H ₇ or P-COOH), 29(C ₂ H ₅), 15(CH ₃), 14(CH ₂)

a. All products except butyric acid were observed for each sample regardless of the temperature or atmosphere.

b. P = parent peak or molecular ion.

c. Also identified by gas chromatography.

d. For straight chain monocarboxylic acids, the parent peak is normally very faint, and the peak at 60 is characteristic of such compounds (Reference 10).

TABLE 9

Gas Chromatographic-Quadrupole Mass Spectral
Analysis of Gases Evolved by Thermal
Decomposition of Adduct

<i>Gas</i>	<i>Concentration, vol %</i>
O ₂	0.06
N ₂	21.6
NO	29.7
N ₂ O	11.4
CO	16.7
CO ₂	31.3
ethene	0.06
propene	0.10
1-butene	<u>12.2</u>
Total	123.1 ^a

^a. Indicates analytical uncertainty.

DENITRATION STUDIES

During denitration of UN solutions, adduct present decomposes when the boiling temperature of the solution is increased sufficiently by evaporation. The decomposition is characterized by foaming and evolution of brown NO_x-containing gases (Figure 8). The studies described below were conducted to determine the effect of various process parameters on adduct decomposition and to better understand the decomposition reaction.

Effect of Heatup Rate on Foaming

Denitrations of UN containing initially 0.2 vol % adduct were conducted to determine the effect of heatup rate on foaming behavior and on the initiation temperature of foaming. Although the data were somewhat scattered (Figure 9), the initiation temperature (10 to 15°C) increased slightly when the heatup rate was increased by a factor of 10. Measurements of initiation temperature were difficult to reproduce; severity of foaming varied and apparently was not related to heatup rate. The heatup rates studied were higher than those anticipated in SRP (0.5 to 1.0°C/min) because of problems with solidification of UN at low

heatup rates in laboratory-scale equipment. SRP tests have shown that solidification is not a problem in plant equipment at heatup rates of 0.5 to 1°C/min.

FIGURE 8. Foaming During Denitration of Uranyl Nitrate Solution Containing 0.2 vol % Adduct

FIGURE 9. Effect of Heatup Rate on Initiation Temperature of Foaming

Effect of Adduct Concentration

Test denitrations were conducted with reagent-grade UN solutions containing different amounts of adduct (Table 10) to determine the temperature at which adduct decomposition began and to define the effect of adduct concentration on foaming. In addition, denitrations of actual SRP solutions were conducted to determine the expected foaming behavior during resumption of A-Line processing (Table 11).

With both synthetic and SRP solutions, no foaming was observed at temperatures ($<130^{\circ}\text{C}$) corresponding to the SRP evaporation steps. However, in the temperature range (~ 130 to 200°C) corresponding to the denitration step, foaming was significant with the reagent-grade UN solutions even at 0.04 vol % adduct. Contents foamed out of the container in experiments containing 0.5 to 1.0 vol % adduct. SRP solutions that had been filtered and processed through a coalescer unit to remove most organic material foamed very little, if at all (Table 11). In all cases, adduct decomposition was complete before denitration of UN began at an observable rate.

These tests indicated that adduct concentrations must be maintained as low as possible (certainly <0.5 vol %) to control foaming. Recent SRP operating experience indicates that <0.1 vol % adduct in hydrate evaporator feed can be consistently achieved, and that antifoam additions are required in only $\sim 10\%$ of the denitrations. The effect of different amounts of antifoam is discussed in the following section.

Effect of Antifoam

Denitration tests were conducted with SRP UN solutions to determine the number and volume of antifoam additions required for foaming control. As shown in Table 11, 4 to 6 antifoam additions of 25 μl (equivalent to the 75 ml recommended for use on plant scale) had little or no effect on the maximum foam height during denitration tests with solutions containing 0.1 to 0.2 vol % adduct. Much larger volumes of antifoam (100 to 200 μl) were required to significantly reduce the level of foaming; no volume tested completely eliminated foaming. Foam momentarily receded after each antifoam addition, but quickly recovered. Thus, the timing of the additions is important, and in these tests, the antifoam additions were separated by approximately equal time intervals. For SRP solutions containing 0.1 to 0.2 vol % adduct, these results indicate that 4 to 6 additions of ~ 500 ml of antifoam will be required during denitration to significantly reduce foaming. With solutions containing lower adduct concentrations (0.02 to 0.08 vol %), recent SRP experience has shown that one or two antifoam additions of 50 to 75 ml reduce foaming significantly.

TABLE 10

Denitration of Uranyl Nitrate with Varying Amounts of Adduct Present

Adduct, vol %	Temperature, °C		Return of Colorless Fumes ^b
	Onset of Foaming	Onset of Brown Fumes ^a	
0	None	-	150
0.04	134	-	150
0.10	146	150	160
0.20	152	167	186
0.50	154	156	180
0.50	143	152	>170
0.75	143	153	174
1.00	140	146	174

- a. The fumes containing NO₂ result from the decomposition of adduct rather than from denitration of uranyl nitrate.
- b. The colorless fumes were evolved until ~200°C was reached, and denitration of uranyl nitrate reached an observable rate.

TABLE 11

Characterization of Foaming During Denitration of SRP Uranyl Nitrate Solutions

Description of Solution ^a	Organic Content, vol % ^b	Antifoam Additions		Temperature Range of Foaming, °C	Maximum Foam Height, in. ^c
		Number	Volume of Each, µl		
E-1-3 Solution	n.a., 0.010	0	0	145-165	5/8
		6	25	160-175	5/8
		6	100	148-184	3/8
S-1-8 Solution with organic material added	0.18, 0.11	0	0	152-178	2-1/4
		4	25	150-186	1-7/8
		1	100	155-183	1-7/8
		4	100	146-180	1-1/4
		4	200	148-180	3/4
S-1-8 Solution processed through a coalescer unit	0.03, 0.008	0	0	-	0
S-1-9 Solution processed through a coalescer unit	0.04, 0.008	0	0	140-166	<1/8
C-1-1 Solution processed through a coalescer unit	0.03, 0.006	0	0	-	0

- a. Tank E-1-3 contains dilute uranyl nitrate solution (90 to 100 g µ/l); Tanks S-1-8, S-1-9, and C-1-1 contain solution concentrated to ~400 g µ/l.
- b. The first value was determined by SRP; the second value was measured at SRL using the phosphate method; n.a. indicates not analyzed.
- c. The depth of the solution was ~1/2 in. when foaming began; the indicated foam height was measured from the surface of the uranyl nitrate solution to the highest point that foam reached.

Analysis of Gaseous Decomposition Products

Gas chromatographic (GC) analyses were conducted of gases emitted from denitrations of UN during adduct decomposition. Gas samples were obtained by the following methods:

- Water displacement (Table 12)
- Quenching a denitration during foaming at $\sim 150^{\circ}\text{C}$ and sealing the vessel (Table 13)
- Withdrawing samples with a syringe from the gases above a denitration at various temperatures (Tables 14 and 15)

The major inorganic gases observed were N_2 , N_2O , NO , CO_2 , and CO . NO_2 was observed visually, but not with GC analysis; it was produced either directly during adduct decomposition or indirectly by reaction of NO with air. NO_2 was not detected by GC analysis probably because of reaction with water during collection or reaction with water on the GC column. NO_2 did not react completely with water during collection because gases collected by water displacement (Table 12) were analyzed soon after collection, and the brownish color of NO_2 was definitely observed in the sample injected into the GC. The total concentration of inorganic gases roughly equaled 100% with an estimated uncertainty of $\pm 10\%$. Thus, 10% is considered as an upper limit on the NO_2 concentration.

As shown in Table 15, the concentration of flammable compounds in the evolved gases was very low ($< 1 \text{ vol } \%$). Analyses of the samples withdrawn from denitration reactions at various temperatures (Tables 14 and 15) showed that the concentrations of both organic and inorganic decomposition gases decreased at 160 to 180°C . This decrease indicates that most of the adduct had decomposed and correlates with the observed cessation of foaming.

The adduct probably decomposes during denitration of UN in the following steps: 1) decomposition of adduct to form free TBP and TBP degradation products such as butyl nitrate and butyric acid, and 2) oxidation of most TBP and TBP degradation products to CO and CO_2 . The oxidation step is beneficial to denitrator safety in one respect because the denitrator off-gas is less flammable. However, as discussed in a following section, the oxidation releases heat which could accelerate the decomposition reaction.

TABLE 12

Analysis of Denitration Off-Gas Collected Over Water^a
(5Å Molecular Sieve Column)

Compound	<i>Concentration in Off-Gas for Duplicate Samples</i>	
	<i>Sample 1</i>	<i>Sample 2</i>
O ₂	0.7	0.7
N ₂	52.8	57.0
NO	25.3	20.8
N ₂ O	10.6	10.7
CO	2.5	3.9
CO ₂	8.1	7.1
ethane	4 ppm	4 ppm
propane	5 ppm	-

a. Denitration reaction mixture contained initially
1 vol % adduct.

TABLE 13

Analysis of Gases Obtained by Quenching A Denitration
Denitration Reaction at 156°C and Sealing the Vessel^a
(5Å Molecular Sieve Column)

Compound	<i>Concentration of Off-Gas, vol %</i>	
	<i>100°C^b</i>	<i>150°C^b</i>
O ₂	5.3	4.6
N ₂	58.3	56.6
NO ^c	0	0
N ₂ O	22.7	25.4
CO	2.9	0.7
CO ₂	10.8	12.7

a. Denitration reaction mixture contained initially
1 vol % adduct.

b. Reaction mixture was reheated to the indicated
temperatures before sampling gas.

c. Gas mixture was not analyzed until several hours
after collection. NO may have been converted to
undetectable NO₂ during this waiting period.

TABLE 14

Analysis of Denitration Off-Gas at Various Temperatures
(5Å Molecular Sieve Column)

Compound	Concentration in Off-Gas, vol % ^a		
	146°C	160°C	178°C
O ₂	0.7	16.0	17.9
N ₂	50.6	82.0	81.5
NO	9.8	trace	trace
N ₂ O	18.9	2.8	0.4
CO	1.5	0	0
CO ₂	18.3	1.7	0.2
ethane	trace	-	-
	99.8	102.5	100.0

a. Gas samples were withdrawn from the same denitration reaction containing (initially) 1 vol % adduct when the reaction reached the indicated temperatures.

TABLE 15

Analysis of Organic Compounds in Denitration
Off-Gas at Various Temperatures (Carbowax-
20M Terephthalic Acid Column)

Compounds	Concentration of Gas, ppm ^a		
	150°C	160°C	170°C
n-butyl nitrate ^b	-	400	60
butyric acid ^c	800	900	1000
total organic	2400	6000	2900

a. Gas samples were withdrawn from the same denitration reaction containing initially 1 vol % adduct when the reaction reached the indicated temperature.

b. Identified by GC retention data and QMS.

c. Identified by GC retention data only.

CALCULATION OF MAXIMUM FLAMMABLE GAS EVOLUTION DURING DENITRATION

With existing A-Line equipment, small quantities of adduct cannot be prevented from reaching the denitrators. Therefore, safe operation of A-Line can be achieved only by operating the denitrators in such a way that any adduct present is decomposed slowly, under controlled conditions. The three basic process parameters which must be controlled for safe operation are 1) quantity of adduct present, 2) heatup rate, and 3) dilution air that enters the off-gas flow. The quantity of adduct present controls the volume of flammable gas that can be produced; the heatup rate controls the rate of adduct decomposition and, therefore, the rate of flammable gas evolution; enough air must be added to the off-gas flow to dilute the flammable gases below the lower limit of flammability. Flammability data for several pertinent compounds are shown in Table 16. Based on the lowest expected value, 1.5 vol % flammable gas is a suitable value for process design purposes.

TABLE 16

Flammability of Adduct Decomposition Products in Air at Atmospheric Pressure

Compound	Limit of Flammability, vol %		Minimum Autoignition Temperature, °C
	Lower	Upper	
n-butane	1.86	8.41	405
n-butyraldehyde	-	-	230
n-butyric acid	2.1	-	450-552
n-butanol	1.7	12	345
n-butyl nitrate	1.5 ^a	-	<190 ^a
1-nitrobutane	<2 ^a	-	-
ethane	3.0	12.4	515
propane	2.1	9.5	450

a. Estimated from values for the appropriate methyl, ethyl, propyl and pentyl compounds.

b. Data from References 11-15.

A computer program (see the Appendix) was developed to calculate the maximum vol % of flammable gas (as butyl compounds) at any time during a denitration. These calculations are based on decomposition rate constants for the first adduct reaction, the quantity of adduct present, formation of 3 moles of butyl compound per mole of TBP, the added air as expressed in the off-gas flow rate, and the heatup rate (assumed to remain constant). The following operating conditions were assumed in these and succeeding denitrator safety calculations:

- Each denitrator batch contains 2000 lb of uranium.
- Volume of each hydrate evaporator feed batch is 600 gal.
- Adduct is limited to 0.2 vol % or 1.2 gal (corresponds to 3820 g TBP).
- Specific gravity of adduct is 1.467.
- Dilution air enters the denitrator at room temperature of 25°C and is expanded to a volume corresponding to the off-gas temperature.
- The off-gas temperature is assumed to be 60°C less than the pot contents temperature (based on A-Line tests).

Off-gas analyses indicated that adduct is not converted completely to flammable gases during denitration or during thermal decomposition of pure adduct. Therefore, use of maximum theoretical conversion of TBP to butyl compounds (3 moles of butyl compound per mole of TBP) incorporates considerable conservatism into the calculations.

The results can be applied to illustrate the effect of the heatup rate on gas evolution (Figure 10). Lower heatup rates are advantageous because the flammable gases are evolved over a longer time interval, and less air per unit time is required for dilution. Also, larger quantities of adduct can be decomposed safely for the same reason. Because gas evolution is directly proportional to the quantity of adduct present (Figure 6), at 0.5°C/min heatup rate and 100 cfm dilution air flow, greater than 3 gal of adduct can be decomposed safely. Conversely, at 2°C/min heatup rate and 100 cfm dilution air flow, the lower limit of flammability is nearly reached with 1 gal of adduct.

The peak concentrations of butyl compounds in the off-gas were calculated for different heatup rates and dilution air flows (Figure 11). In these calculations, the heatup rate has been assumed to remain constant. However, as discussed in the following section, exothermic reactions could heat the melt and increase the heatup rate during denitration.

FIGURE 10. Maximum Concentration of Butyl Compounds in Denitrator Off-Gas

Assumptions

- 1 gal adduct
- 100 cfm dilution air at 25°C (expanded to 60°C below temperature of pot contents for dilution calculation)
- 3 moles of butyl compounds produced per mole of TBP

EFFECT OF SELF-HEATING ON THE ADDUCT DECOMPOSITION RATE

Laboratory studies have demonstrated that a portion of the TBP present (as adduct) in uranyl nitrate solutions undergoing thermal denitration is oxidized by nitrate in the condensed phase. This oxidation is exothermic and can affect the heat balance of the system. Oxidation also has the effect of diluting the flammable organic gases originating from thermal decomposition or chemical attack on TBP with a large volume of nonflammable gaseous combustion products: CO_2 , CO , H_2O , and nitrogen and its oxides. From the standpoint of safety, these effects are opposed. Additional heat added to the denitration melt increases its rate of heating and thereby accelerates further TBP decomposition. However, the unreactive gases generated decrease the quantity of airflow through the denitration vessel that would be required to dilute the organic gases below the lower flammable limit. These effects were calculated to determine which predominates.

FIGURE 11. Peak Concentration of Butyl Compounds in Denitrator Off-Gas per Gallon of Adduct

Calculations assume that: 1) dilution air enters at 25°C and is expanded to a volume corresponding to 60°C below the temperature of the pot contents, and 2) 3 moles of butyl compounds are produced per mole of TBP

The extent of TBP oxidation under SRP conditions is unknown and probably is a function of pot geometry and stirring conditions; thus, extent of oxidation cannot be determined from laboratory studies. Laboratory studies have not in fact detected any heat release from oxidation. Therefore, the heat and gas evolved for various degrees of oxidation were calculated (Table 17). The calculations assume that the model conditions are those stated in the previous section (3820 g of TBP in a one-ton uranium batch), and that TBP oxidation releases as much heat per g of TBP oxidized as the reaction

From published data, ΔH for this reaction is -1634 kcal/mole.^{16,17} The volume of combustion products generated is assumed to be 20 mol/mol TBP, ignoring steam and assuming that at least a small amount of nitrogen is emitted as oxides. The temperature rise is calculated assuming the heat capacity is 0.32 cal/g °C;¹⁸ the actual heat capacity varies with the stage of denitration. However, at a constant heating rate, the melt temperature increases about linearly with time, indicating a nearly constant heat capacity. The denitrator is operated to heat-up at a rate not exceeding 1°C/min over the critical range from 120 to 200°C. Table 17 shows that considerable oxidation must occur to have a major effect in accelerating this heating rate. To estimate this effect, the TBP decomposition rate was calculated for various amounts of TBP oxidation in the melt. The calculation assumed a homogeneous dispersion of adduct in the liquid, a heating rate of 1°C/min, and the thermal parameters previously given. The heat-up rate, the mass of the denitration batch, and the specific heat were used to derive an effective heat input into the system; this heat input was then compared with the heat added by reaction (Table 18). The following conclusions can be derived:

- Oxidation of TBP increases the heating rate, principally at the higher temperature.
- The temperature at which the maximum TBP decomposition occurs shifts upward; for >50% oxidation, it can be above 200°C.
- The effect of dilution by combustion products overwhelms that of the increased heating rate, and the amount of airflow required for dilution decreases steadily as the amount of oxidation increases.

The volume of dilution air required to dilute the maximum volume of flammable gases (3 moles of butyl compounds per mole of TBP) below the lower limit of flammability will be adequate at any degree of TBP oxidation. This conclusion is valid so long as the TBP concentration is limited, and the TBP is well mixed with the aqueous phase during the denitration step. Revised A-Line operating procedures have been written to ensure that safe operating conditions will be maintained.

TABLE 17

Calculated Heat and Gas Generated by TBP Oxidation in A-Line Denitrator

TBP Oxidized, %	0	25	50	75	100
Flammable Gas Emitted, mol/mol TBP	3	2.25	1.5	0.75	None
Combustion Products Emitted, mol/mol TBP	0	5	10	15	20
Heat Generated per g Melt, cal	0	3.3	6.6	9.9	13.2
Temperature Rise, °C	0	10.3	20.6	30.9	41.2
Total Gas Volume Generated per ton U, ft ³ (at 120°C)	49	118	187	257	326
Combustible Content of Emitted Gas, %	100	31	13	4.8	None
Dilution Factor Required (to 1.5%)	66.7	20.7	8.7	3.2	-
Volume of Room Air Required to Dilute below 1.5%, ^a ft ³ (at 120°C)	3270	2450	1630	820	-
Volume of Room Air Required, ft ³ (at 25°C)	2480	1860	1240	620	-

a. Lower explosion limit for butyl nitrate. See Table 16.

TABLE 18

Calculated Decomposition Rates and Dilution Requirements for Various Degrees of TBP Oxidation

(Assumptions: 3820 g TBP/ton U; nominal heating rate, 1°C/min)

TBP oxidized, %	0	25	50	75	100
Maximum heating rate, °C/min	1.0	1.3	1.8	2.4	3.5
Maximum TBP decomposition rate, g/min	92	111	134	168	217
Temperature of maximum decomposition rate, °C	191	194	198	205	212
Air required to dilute below flammable limit, ft ³ /min at 25°C	63	55	44	27	None

APPENDIX - COMPUTER PROGRAM FOR DENITRATOR OFF-GAS CALCULATIONS

(MAY 72)

CS/360 FORTRAN H

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COMPILER OPTIONS - NAME= 4AIN,OPT=C0,LINECNT=58,SIZE=0000K,
                      SOURCE,EBCDIC,NGLIST,NODECK,LOAD,MAP,NOEDIT,NOXREF
C   PROGRAM OFFGAS
C   TEMP=CENTIGRADE
C   TEMPK=ABSOLUTE
C   OGTEMP=OFFGAS TEMPERATURE (ASSUMED TO BE 60C LESS THAN POT)
C   TINVS=INVERSE OF ABSOLUTE TEMPERATURE
C   TLNK=NATURAL LOG OF RATE CONSTANT
C   TLOGK=LOG OF RATE CONSTANT
C   TK=RATE CONSTANT
C   HALFT=HALF LIFE OF REACTION
C   EACT=ACTIVATION ENERGY FROM SLOPE OF LOG K VS 1/T PLOT
C   YINTCP=Y INTERCEPT OF LOG K VS 1/T PLOT
C   TEMPI=LOWER END OF TEMPERATURE RANGE OF INTEREST
C   N=NUMBER OF TEMPERATURES IN ONE DEGREE INTERVALS
C   VOLADD=VOLUME OF ADDUCT IN DENITRATOR IN GALLONS
C   AMTADD=WEIGHT OF ADDUCT IN DENITRATOR AT TIME T IN LBS.
C   TLOGAD=LOG OF WEIGHT OF ADDUCT
C   TLNADD=NATURAL LOG OF WEIGHT OF ADDUCT
C   HTRATE=HEAT UP RATE FOR DENITRATOR
C   FLOWRT=OFF GAS FLOW RATE BEING APPLIED TO DENITRATOR IN CFM
C   AMTDCP=AMOUNT OF ADDUCT DECOMPOSED IN EACH TIME INTERVAL
C   VOLGAS=VOLUME OF GAS EVOLVE DURING EACH TIME INTERVAL
C   VOLPCT=VOLUME PERCENT OF FLAMMABLE GAS IN DENITRATOR OFF GAS
C   TIME=TIME ELAPSED FROM INITIAL TEMPERATURE TO PRESENT TEMPERATURE
C   TMDCP=TIME ALLOWED FOR DECOMPOSITION AT EACH TEMPERATURE
REAL*8 TEMP(500),TEMPK(500),TINVS(500),TLNK(500),TLOGK(500),
1  TK(500),HALFT(500)
REAL*8 AMTADD(500),TLOGAD(500),TLNADD(500),AMTDCP(500),
1  VOLGAS(500),VOLPCT(500),TIME(500),OGTEMP(500)
2  READ 2,EACT,YINTCP,TEMPI,N
2  FORMAT(3F10.0,I5)
3  TEMP(1)=TEMPI
4  DO 5 I=2,N
5  TEMP(I)=TEMP(I-1)+1.0
6  DO 13 I=1,N
7  TEMPK(I)=TEMP(I)+273.0
8  TINVS(I)=1.0/TEMPK(I)
  OGTEMP(I)=TEMPK(I)-60.0
9  TLOGK(I)=-(EACT/4.583)*(TINVS(I))+YINTCP
10 TLNK(I)=TLOGK(I)*2.303
11 TK(I)=DEXP(TLNK(I))
12 HALFT(I)=0.693/TK(I)
13 CONTINUE
  PRINT 50
50 FORMAT(1X,13HTEMPERATURE C,5X,3H1/T,10X,5HLOG K,10X,1HK,7X,
2  13HHALF LIFE,HRS)
14 DO 17 I=1,N
15 PRINT 16,TEMP(I),TINVS(I),TLOGK(I),TK(I),HALFT(I)
16 FORMAT(4X,F5.0,6X,F10.6,4X,F10.6,3X,F10.6,4X,F10.6)
17 CONTINUE
  READ 80,NORUNS
80 FORMAT(I5)
DO 42 J=1,NORUNS
18 READ 19,VOLADD,HTRATE,FLOWRT
19 FORMAT(3F10.0)

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20 AMTADD(1)=VCLADD*12.228
21 TMDCP=1.0/HTRATE
22 COUNT=1.0
23 TIME(1)=0.0
24 TLOGAD(1)=DLOG10(AMTADD(1))
25 AMTDCP(1)=0.0
26 VOLGAS(1)=0.0
27 VOLPCT(1)=0.0
28 TLNADD(1)=DLOG(AMTADD(1))
29 DO 37 I=2,N
30 TIME(I)=TMDCP*COUNT
31 COUNT=COUNT+1.0
32 TLOGAD(I)=-(TK(I)/(2.303))*(TMDCP/50.0)+TLOGAD(I-1)
33 TLNADD(I)=TLOGAD(I)*2.302585090 00
34 AMTDCP(I)=(DEXP(TLNADD(I-1))-(DEXP(TLNADD(I))))
C   THE NEXT STATEMENT CONVERTS WEIGHT OF ADDUCT TO VOLUME BUTYL
C   COMPOUNDS ALL CONVERSION FACTORS ARE COMBINED.
C   THE NEXT STATEMENT CONVERTS THE VOLUME OF OFFGAS TO VOLUME
C   PERCENT AT THE ESTIMATE OFFGAS TEMPERATURE (POT TEMPERATURE-60C)
35 VCLGAS(I)=AMTDCP(I)*GTTEMP(I)*0.0085154
C   THE DILUTION AIR IS CONVERTED TO THE OFFGAS TEMPERATURE
36 VOLPCT(I)=(VOLGAS(I)/(FLOWRT*TMDCP*(GTTEMP(I)/298.)))*100.0
37 AMTADD(I)=DEXP(TLNADD(I))
PRINT 100
100 FORMAT(1H1)
PRINT 60,VOLADD,HTRATE,FLOWRT
60 FORMAT(4X,25HINITIAL VOLUME OF ADDUCT=,F4.1,1X,3HGAL,4X,13HHEAT UP
4 RATE=,F5.2,1X,5HC/MIN,4X,13HFLW RATE=,F5.0,1X,3HCFM)
PRINT 65
65 FORMAT(1H0)
PRINT 70
70 FORMAT(4X,8HTIME,MIN,4X,11HTEMPERATURE,4X,10HADDUCT,LBS,4X,
3 14HDECOMPOSED,LBS,4X,13HGAS VOLUME,CF,4X,14HVOLUME PERCENT)
38 DO 41 I=1,N
39 PRINT 40,TIME(I),TEMP(I),AMTADD(I),AMTDCP(I),VOLGAS(I),VOLPCT(I)
40 FORMAT(F10.1,4X,F10.1,6X,F10.4,5X,F10.4,7X,F10.4,9X,F10.6)
41 CONTINUE
42 CONTINUE
STOP
END

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