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PROCESS ENGINEERING DESIGN FOR MANUFACTURE OF GUANIDINE NITRATE

HERCULES, INC.

PREPARED FOR
PICATINNY ARSENAL

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HERCULES INCORPORATED
KENVIL, NEW JERSEY

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Final Report

APPENDICES FOR VOLUME I

(Unclassified - Department of the Army)

N. W. Steele
J. A. Doyle
M. G. Whippen

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HERCULES INCORPORATED
Wilmington, Delaware 19801

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APPENDIX I - PHASE I

LABORATORY, ENGINEERING, ECONOMIC AND TECHNOLOGY STUDIES

APPENDIX I-1

PACKED BED REACTOR MODEL

In this section, a detailed description of the packed bed reactor model is given. The method of numerical solution of the ordinary and partial differential equations is also treated.

Model Development

The model for the packed bed reactor is based upon material and energy balances for the system. By considering an annular ring of differential size, the following ordinary and partial differential equations for the concentrations and temperature at every point in the reactor may be written:

$$(1)\quad \frac{dN_{GN}}{dz} = \frac{1}{L}\left[R_{GN}\cdot\rho_B\cdot A - N_{GN}\frac{dL}{dz}\right]$$

$$(2)\quad \frac{dN_{XL}}{dz} = \frac{1}{L}\left[R_{XL}\cdot\rho_B\cdot A - N_{XL}\frac{dL}{dz}\right]$$

$$(3)\quad \frac{dN_{AN}}{dz} = \frac{1}{L}\left[R_{AN}\cdot\rho_B\cdot A - N_{AN}\frac{dL}{dz}\right]$$

$$(4)\quad \frac{dL}{dz} = R_{XL}\cdot\rho_B\cdot A$$

(5) $$\frac{dG}{dZ} = 3 \cdot R_{GN} \cdot \rho_B \cdot A$$

(Gas actually ≈ NH_3 + CO_2 & not AC; $R_G = 3 K_{ur}$)

(6) $$K_E \left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right] - \Phi \cdot \frac{\partial T}{\partial Z} - \Psi \cdot (T - T_1)$$

$$= H_R \cdot R_{GN} \cdot \rho_B$$

where

(7) $$R_{GN} = N_U \cdot N_{AN} \cdot k^0_{GN} \, e^{-E_{GN}/RT_{AVG}}$$

(8) $$R_U = - N_U^2 \cdot N_{AN} \cdot k^0_U \, e^{-E_U/RT_{AVG}}$$

(9) $$R_{AN} = - R_{GN}$$

(10) $$\Phi = C_L \cdot L' + C_G \, G'$$

(11) $$\Psi = C_L \cdot \frac{dL'}{dZ} + C_G \frac{dG'}{dZ}$$

(12) $$N_{GN} + N_U + N_{AN} = 1$$

(13) $$T_{AVG} = \frac{2\pi}{A} \int_0^{r_T} T(r) \, r \, dr$$

The definition of the variables used in these equations can be found in the List of Symbols included at the end of this section.

Equations (1), (2), and (3) are the material balances for guanidine nitrate, urea, and ammonium nitrate and describe the variation in mole fraction for each component in the axial direction. The mole fractions have been assumed uniform in the radial direction. This is a reasonable assumption in packed bed operations since the catalyst particles contribute to a lateral movement of fluid leading to mixing in the radial direction. In addition, the time associated with convective transport of material in the axial direction will far outweigh any contribution due to radial concentration gradients. The first term on the right-hand-side of Equations (1), (2), and (3) accounts for the production or removal of material by chemical reaction. The rate expressions used here and defined by Equations (7), (8), and (9) are those obtained through the analysis of the kinetic experiments of this project as presented in last month's report. The second term in the material balance equations accounts for the effect of the change in melt volume due to chemical reaction on the variation in mole fraction with axial position. Equation (4) is obtained by summing Equations (1), (2), and (3) and recalling that Equation (12) also applies. Equation (5) describes the rate of production of gas as a function of axial position and assumes that the gas is generated only by those reactions that produce guanidine nitrate, and that an insignificant amount of gas is generated by side reactions. This is in keeping with the experimental results of this project in which no gas other than that going to ammonium carbamate was detected.

Equation (6) is the energy balance for the packed bed reactor and describes both the radial and axial variation in temperature. Axial and radial temperature profiles are important, since the reaction rates are a strong function of temperature. The yields, conversions, and concentration profiles will be directly affected. In addition, the maximum allowable radial temperature difference will determine the maximum diameter of the packed bed reactor.

The first term in Equation (6) accounts for the energy transfer in the radial direction by conduction. All resistances to heat transfer in the radial direction inside the bed are included in the effective thermal conductivity, K_E. These resistances include thermal resistance at the wall, thermal resistance of the particles and of the contact area between the particles, thermal resistance of the liquid and gas between particles, the thermal resistance from the particles to the liquid, thermal resistance from the liquid surrounding the particles to the bulk of the gas, and the thermal resistance of both liquid and gas at rest and in motion. In a system such as the guanidine nitrate system, in which gas is generated continuously along the length of the reactor, the effective thermal conductivity will vary with axial position. A correlation due to Weekman and Myers (Ref. 4) is used to predict the effective thermal conductivity at each axial position and is discussed below.

The second term in the energy balance, $\phi \partial T/\partial Z$, accounts for the thermal energy transported by flow in the axial direction. An expression for ϕ is given in Equation (10) as a function of the specific heats of the liquid and gas and the molar flow rates per unit cross-section for the liquid and gas. The third term of Equation (6) describes the contribution to the temperature change due to the change in volume of the melt and gas because of chemical reaction. For this term, the datum temperature was selected for convenience as the feed temperature. An expression for ψ is given in Equation (11).

The final term of the energy balance is the heat generated by chemical reaction. The heat of reaction and the rate are assumed to be those associated with the guanidine nitrate reaction.

To evaluate the reaction rate expressions for use in the material balance equation, the average radial temperature at each axial position was calculated by Equation (13).

The set of boundary conditions necessary for the solution of these equations is:

1. at $Z = 0$

$$x_{GN} = x_{GN}^{f}$$

$$x_{U} = x_{U}^{f}$$

$$x_{AN} = x_{AN}^{f}$$

$$L = L^{f}$$

$$G = G^{o} = 0$$

$$T(r) = T^{f} \quad \text{for all } r$$

where superscript f refers to feed conditions.

2. at $r = 0$

$$\frac{\partial T}{\partial r} = 0 \quad \text{for all } Z$$

3. at $r = r_T$

$$2\pi r_T K_E \left.\frac{\partial T}{\partial r}\right|_{r_T} = - U (T_W - T_1) 2\pi r_m$$

for all Z

The presence of the flowing gas phase in the guanidine nitrate system greatly increases the effective thermal conductivity in the packed bed reactor when compared to the effective thermal conductivity that would be expected from the liquid phase alone. The primary effect of the gas is to increase the velocity of the liquid phase. Weekman and Myers (Ref. 4) have proposed and tested the following correlation for predicting the effective thermal conductivity of a packed bed with concurrent gas-liquid flow:

$$\frac{K_E}{k_l} = \frac{7.03}{k_l} + 0.000285 \, (N'_{RE})_l \, (N_{PR})_l$$

where $(N'_{RE})_l$ is the Reynolds number based on the actual cross-section area available for flow:

$$(N'_{RE})_l = \frac{D_t \, L''}{\mu_l \, \epsilon \, R_L} \, .$$

R_L is the fraction of the void volume occupied by the liquid. This definition of Reynolds number follows directly from the liquid mass velocity based on the actual area available for flow of the liquid:

$$L''_{ACT} = \frac{L''}{\epsilon \, R_L}$$

Weekman and Myers have tested this correlation for various size spherical packings ranging from 0.149" to 0.255" diameter and over a wide range of gas and liquid flow rates. They found that this single correlation satisfactorily predicted the thermal behavior of the packed bed. They observed that the amount of heat transferred did not appear to be a function of the tube to particle diameter ratio when this ratio was varied from 11.8 to 20.0. The Reynolds number was therefore based upon the tube diameter. For the Houdry silica beads used in this project, the tube-to-diameter ratio for a 4" column would be approximately 16, which is within the range tested in Ref. 4.

To complete the model, R_L, the fraction of void volume occupied by the liquid must be predicted at all axial positions. This can be done by utilizing the correlation proposed by Larkins et al. (Ref. 3). In this work, they were able to relate the two-phase friction loss for flow of a liquid and gas through a packed bed to the single phase losses and the fraction of the cross-section occupied by the liquid. For a variety of packings and with gas-liquid systems having a wide range of fluid properties, the following equation was found to apply:

$$\log_{10} R_L = -0.774 + 0.525 (\log_{10} \chi) - 0.109 (\log_{10} \chi)^2$$

where

$$\chi = \sqrt{\delta_l / \delta_g}$$

The terms δ_l and δ_g are the friction losses for the single phase flows of the liquid and gas. These can be predicted by the Ergun equation

(Ref. 1) for pressure drops in packed beds:

$$\delta \cdot \left(\frac{g_c \rho D_p^3}{\mu^2}\right)\left(\frac{\epsilon}{1-\epsilon}\right)^3 = N_{RE}\left(\alpha + \beta N_{RE}\right)$$

where
$$N_{RE} = \frac{D_p L''}{\mu(1-\epsilon)}$$
$$\alpha = 150$$
$$\beta = 1.75$$

The ratio of the liquid to gas phase losses will then equal:

$$\frac{\delta_l}{\delta_g} = \frac{N_{REl}\left(\alpha + \beta N_{REl}\right)\rho_g \mu_l^2}{N_{REg}\left(\alpha + \beta N_{REg}\right)\rho_l \mu_g^2}$$

Numerical Solution

The mathematical model equations were solved on an EMR 6130 digital computer. The ordinary differential equations, Equations (1) through (5), were integrated by utilizing a fourth-order Runge-Kutta routine (Ref. 2). The energy equation however is a partial differential equation and a finite difference method must be used. A Crank-Nicholson 6-point implicit form (Ref. 2) was utilized in generating the solution to the distributed parameter system. This technique was selected over the singular explicit methods because of its increased accuracy and because of its property of guaranteeing numerically stable solutions.

The step sizes and mode identifications are defined in Figure A-1. In using the Crank-Nicholson method, the temperature derivatives are defined as follows:

$$\frac{\partial T}{\partial z} = \frac{T_{n,s+1} - T_{n,s}}{k}$$

$$\frac{\partial T}{\partial r} = \frac{1}{4h}\left[\left(T_{n+1,s+1} - T_{n-1,s+1}\right) + \left(T_{n+1,s} - T_{n-1,s}\right)\right]$$

$$\frac{\partial^2 T}{\partial r^2} = \frac{1}{2h^2}\left[\left(T_{n+1,s+1} - 2T_{n,s+1} + T_{n-1,s+1}\right)\right.$$

$$\left. + T_{n+1,s} - 2T_{n,s} + T_{n-1,s}\right)\right]$$

$$T = \frac{1}{2}\left(T_{n,s+1} + T_{n,s}\right)$$

When these difference equations are substituted into Equation (6) and the boundary conditions at $r = 0$ and $r = r_T$ included, a set of tridiagonal linear equations is obtained of the form:

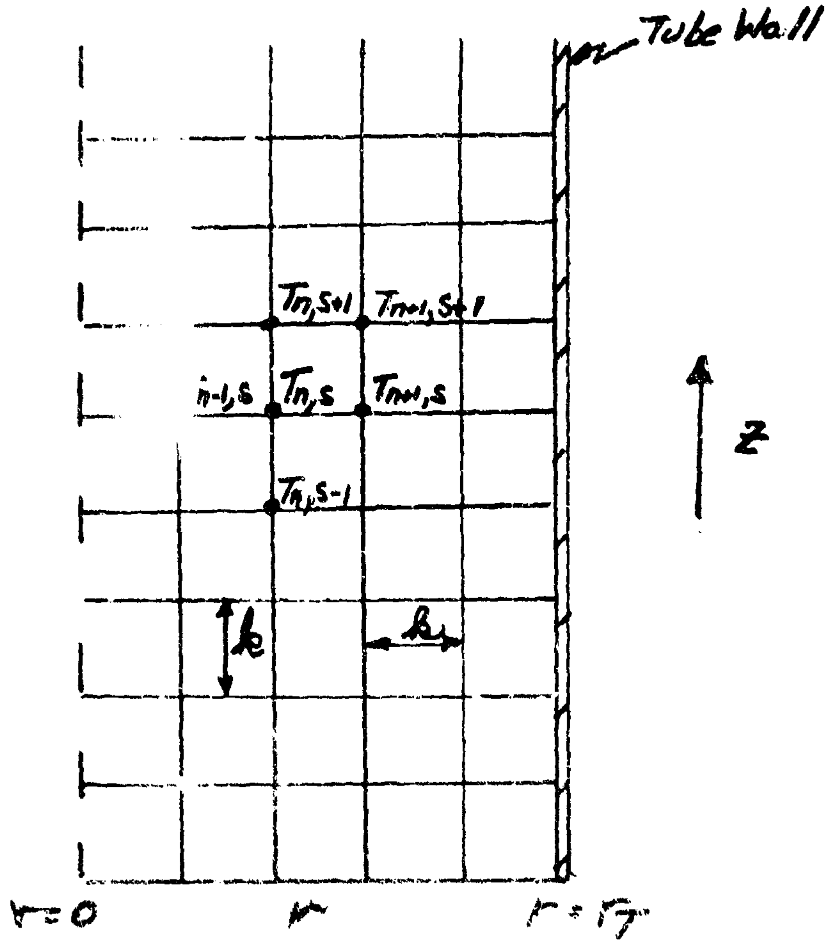

Figure A-1. Description of Nomenclature for Crank-Nicholson Numerical Integration Method

$$C_n \cdot T_{n+1,s+1} + B_n T_{n,s+1} + A_{n-1} T_{n-1,s+1} = D_n$$

where,

$$C_n = \frac{K_E}{2h^2} + \frac{K_E}{4hr}$$

$$B_n = -\frac{K_E}{h^2} - \frac{\delta}{k} - \frac{\psi}{2}$$

$$A_{n-1} = \frac{K_E}{2h^2} - \frac{K_E}{4hr}$$

$$D_n = -T_{n+1,s}\left\{\frac{K_E}{2h^2} + \frac{K_E}{4hr}\right\} - T_{n,s}\left\{\frac{-K_E}{h^2} + \frac{\delta}{k} - \frac{\psi}{2}\right\}$$

$$- T_{n-1,s}\left\{\frac{K_E}{2h^2} - \frac{K_E}{4hr}\right\} + H_R R_{CN} P_E - \psi \cdot T_1$$

for $n = 2, N-1$

and

$$B_1 = -\frac{2K_E}{h^2} - \frac{\delta}{k} - \frac{\psi}{2}$$

$$C_1 = \frac{2K_E}{h^2}$$

$$D_1 = -T_{2,s}\left\{\frac{2K_E}{h^2}\right\} - T_{1,s}\left\{\frac{-2K_E}{h^2} + \frac{\delta}{k} - \frac{\psi}{2}\right\}$$

$$+ H_R R_{GN} \rho_B - \psi T_1$$

$$B(N) = -\gamma \cdot \left(\frac{K_E}{h^2} + \frac{K_E}{hr} \right) - \frac{K_E}{h^2} - \frac{\phi}{h} - \frac{\psi}{2}$$

$$A(NN-1) = \frac{K_E}{h^2}$$

$$D(NN) = -T_{N,S} \left\{ -\frac{K_E}{h^2} + \frac{\phi}{h} - \frac{\psi}{2} \right\} - T_{N-1,S} \left\{ \frac{K_E}{h^2} \right\}$$

$$+ H_R R_{GN} \rho_B - \psi \cdot T_1 - \gamma \cdot T_j \left\{ \frac{K_E}{h^2} + \frac{K_E}{2hr} \right\}$$

where

$\gamma = 2h \cdot$ [illegible]

This tridiagonal matrix set of equations is solved at each axial position by the Thomas (Ref. 2) algorithm.

SYMBOLS
FOR
PACKED BED REACTOR MODEL

A = cross-sectional area of the reactor, inches^2

C_G = specific heat of the gas, calories/(mole)-(°K)

C_L = specific heat of the melt, calories/(mole)-(°K)

D_t = tube diameter, inches

D_P = diameter of catalyst particle, inches

$\frac{d(\cdot)}{dZ}$ = first derivative in the axial direction

E_i = activation energy for component i.

G = molar flow rate of gas, moles/minute

G' = molar flow rate of gas based on the empty tube area, moles/(inch)^2 - minute.

H_R = heat of reaction; taken here as the heat of reaction for guanidine nitrate production, calories/mole

K_E = overall effective thermal conductivity, calories/(min)-(in)-(°K)

k_i^o = specific rate constant for the formation of component i, moles/(gram of catalyst) - (minute)

L = molar flow rate of melt, moles/minute

L' = molar flow rate of melt based on the empty tube area, moles/(inch)^2 - minute

N_{PR} = Prandtl number

N_{RE} = Reynolds number

R_i = rate of formation of component i, moles/(gram of catalyst) - (minute)

R_L = fraction of the void volume occupied by the melt.

r = radial position, inches

r_{lm} = log mean radius = $(r_{OD} - r_T)/\ln(r_{OD}/r_T)$

r_{OD} = outside radius of tube, inches

r_T = radius of the reactor tube, inches

T = temperature, ^{o}K

T_1 = reference temperature; taken here as the feed temperature, ^{o}K.

T_{avg} = area weighted average radial temperature, ^{o}K

T_j = jacket temperature, ^{o}K

T_w = wall temperature, ^{o}K

U = overall heat transfer coefficient at wall calories/(in^2) - (min) - (^{o}C)

x_i = mole fraction of component i.

Z = axial position, inches

ϵ = fraction void space in the bed

ρ = density

ρ_B = bulk packing density of catalyst, grams/cu.in.

μ_l = viscosity of the liquid

$\frac{\partial(\cdot)}{\partial a}$ = first partial derivative in the a direction

ψ = change in melt and gas volume due to chemical reaction - $\frac{cal/min}{(in^3)(^{o}K)}$

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Appendix I-2. LISTING OF PROGRAM

CONTINUOUS PACKED BED REACTOR MODEL

```
C     PACKED BED REACTOR MODEL----V. J. [illegible]
      REAL MOLGAS,MOLLIQ
      DIMENSION COMENT(500)
      DIMENSION A( 4, 4),B( 4),C( 4),ANUM( 4),ADEN( 4)
      DIMENSION AK(6,4),FUNC(6),YY(6)
      DIMENSION YO( 6),Y( 6),YOLD(6)
      DIMENSION CAT(5),WM(6)
      DIMENSION WFRAC(6)
      DIMENSION YWO(6)
      DIMENSION TR1(51),TR2(51)
      DIMENSION PPRINT (10)
      DIMENSION SAVE(3,50)
      COMMON FREQGM,FREQLM,FGN,FL,BULK,VOID,TEMP,AREA,DIAM,U,TC,PI,
     1    HR,CML,CMG,TO,MOLGAS,DPART,R1,R2,US
      KU=2
      REWIND KU
      NN=51
      MM=11
      CMG=10.0
      CML=45.0
      HR=28000.0
      PI=3.1416
C     READ IN THE RUNGE-KUTTA "ORDER" AND THE COEFFICIENTS.
      READ (5,1) M
      DO 101 IROW=1,M
      READ (5,100) (ANUM(I),I=1,M)
      READ (5,100) (ADEN(I),I=1,M)
  100 FORMAT (8F10.5)
      DO 101 IM=1,M
  101 A(IROW,IM)=ANUM(IM)/ADEN(IM)
      READ (5,100) (ANUM(I),I=1,M)
      READ (5,100) (ADEN(I),I=1,M)
      DO 103 IM=1,M
  103 B(IM)=ANUM(IM)/ADEN(IM)
      READ (5,100) (ANUM(I),I=1,M)
      READ (5,100) (ADEN(I),I=1,M)
      DO 102 IM=1,M
  102 C(IM)=ANUM(IM)/ADEN(IM)
      READ (5,1) NCARDS
    1 FORMAT (I10)
      NC=20 * NCARDS
      READ (5,2) (COMENT(I),I=1,NC)
    2 FORMAT (20A4)
      READ (5,6) H,MINT,MTOP,TIME
    6 FORMAT (F20.10,2I10,F20.10)
      READ (5,1) N
      READ (5,3) (YO(I),I=1,N)
    3 FORMAT (4F20.10)
      READ (9,2000)(CAT(I),I=1,5),BULK,VOID,DPART
 2000 FORMAT (5A4,3F10.5)
      READ (9,2001) DIAM,U,TC,R1,R2,US
 2001 FORMAT (8F10.5)
      READ (9,2010) FREQGM,FGL,FREQLM,FL
```

```
2010 FORMAT (4F20.10)
      WM(3)=80.0
      WM(4)=60.0
      WM(5)=122.0
      FEED=Y0(1)
      Y0(1)=Y0(1)*453.6/(Y0(3)*WM(3)+Y0(4)*WM(4)+Y0(5)*WM(5))
      Y0(1)=Y0(1)/60.0
      AN0=Y0(3)*Y0(1)
      D0=Y0(4)*Y0(1)
      GN0=Y0(5)*Y0(1)
      T0=Y0(6)
      TOTAL=0.0
      DO 7010 I=3,5
7010 TOTAL=TOTAL + Y0(I)*WM(I)
      DO 7011 I=3,5
7011 YW0(I)=Y0(I)*WM(I)/TOTAL
      MOLGAS=62.1*(TEMP+273.0)/16.4
      MOLLIQ=3.92
      AREA=PI*DIAM**2/4.0
      WRITE (6,31) (COMENT(I),I=1,NC)
 31   FORMAT (1H1,(2X,20A4))
      WRITE(18,2011)(CAT(I),I=1,5),BULK,VOID
2011 FORMAT(/1X,5A4/3X,'BULK DENSITY ='F6.2,' GRAMS/CU. IN.'/3X,
    1  'VOID FRACTION =',F5.3)
      WRITE (18,2012) DIAM
2012 FORMAT (1X,'TUBE DIAMETER ='F6.2,' INCHES')
      TEMP=Y0(6) - 273.0
      WRITE (18,2013) TEMP
2013 FORMAT (1X,'FEED TEMPERATURE =',F6.1,' C.')
      WRITE (18,3000) TC,U
3000 FORMAT (1X,'JACKET TEMPERATURE =',F6.1,' C.',/1X,
    1  'OVERALL HEAT TRANSFER COEFFICIENT ='F6.2,' CAL./SQ.IN.-MIN.-C.'
    2  )
      TC=TC + 273.0
      WRITE (18,2003)
2003 FORMAT(//1X,'DISTANCE',3X,'MOLAR FLOW RATES',9X,
    1  'MOLE     FRACTIONS',6X,'CONVERSION',5X,'YIELD ',6X,
    2  'TEMPERATURE'/2X,'INCHES',
    3   6X,'MOLES/MINUTE',5X,'AMMONIA',5X,'UREA',3X,'GUANIDINE',
    4  2X,'% ',' READ/',3X,'%',' GN/',6X,'DEG. C.'/
    5  13X,'MELT',7X,'GAS',5X,'NITRATE',13X,'NITRATE',4X,'%',' FEED',5X,
    6  '%   READ'/)
C     PERFORM THE CALCULATIONS USING THE INITIAL CONDITIONS.
      DO 5 I=1,6
 5    Y(I)=Y0(I)
      DO 76 I=1,30
      TR1(I)=Y(6)
 76   TR2(I)=TR1(I)
      ITOTAL=0
      CONV=0.0
      YIELD=0.0
      TEMP= Y(6) - 273.0
      WRITE (18,2004) TIME,( Y(I),I=1,5),CONV,YIELD ,TEMP
```

```
 2004 FORMAT(3F9.3,2X,5(1X,F9.4),7X,F7.1)
      ITAPE=0
      NDEL=NO/5
      ITAPE=ITAPE + 1
      WRITE (KU) TIME,(TR2(J),J=1,NO,NDEL)
      RL=1.0
      RELIO=0.0
      WRITE (KU) RL,RELIO
C     BEGIN THE INTEGRATION.
      ICOUNT=0
      DO 15 ITOTAL=1,NTOP
      DO 91 J=1,6
   91 YOLD(J)=Y(J)
      CALL RUNGE (A,B,C,Y,TIME,H,AK,FUNC,YY,M,N)
      PK=H
      CALL RADIAL (YOLD,Y,WP,TR1,TR2,PK,RL,RELIO,NN)
      TIME=TIME + H
      IF (ITOTAL .EQ. NTOP) GO TO 1010
      IF(ITOTAL .LE. 5) GO TO 1010
      ICOUNT=ICOUNT + 1
      IF(ICOUNT .NE. MINT) GO TO 63
      ICOUNT=0
 1010 CONTINUE
      CONV=(U0 - Y(4)*Y(1))/U0
      YIELD=(Y(5)*Y(1) - GNO)/(U0 - Y(4)*Y(1))
      TEMP= Y(6) - 273.0
      WRITE (IW,2014) TIME,( Y(I),I=1,5),CONV,YIELD,TEMP
      ITAPE=ITAPE + 1
      WRITE (KU) TIME,(TR2(J),J=1,NO,NDEL)
      WRITE (KU) RL,RELIO
 5000 FORMAT (1X,'TR2 =',(10F12.4))
   63 CONTINUE
      DO 80 I=1,N
C     IF(DABS(Y(I)) .LT. 1.0D+60  .AND.   DABS(Y(I)) .GT. 1.0D-60)
C    1     GO TO 80
C     WRITE (6,81)
   81 FORMAT (////,
     1'**************************************************************'
     2//2X,'MAGNITUDE OF Y(I) APPROACHES THE LIMIT OF THE MACHINE.'//
     3'**************************************************************')
C     GO TO 82
   80 CONTINUE
   15 CONTINUE
      WRITE(IW,2015) FEEDW,(YW0(I),I=3,5)
 2015 FORMAT(/1X,'MELT FEED RATE =',F6.2,' LB./HR.'/
     1  1X,'FEED WEIGHT FRACTIONS =  AMMONIUM NITRATE =',F7.4,
     2  /38X,'UREA =',F7.4/25X,'GUANIDINE NITRATE =',F7.4)
      PROD=60.0*Y(1)*(Y(3)*WM(3)+Y(4)*WM(4)+Y(5)*WM(5))/453.6
      TOT=0.0
      DO 2035 I=3,5
      WFRAC(I)=Y(I)*WM(I)
 2035 TOT=TOT + WFRAC(I)
      DO 2040 I=3,5
```

```
 2040 WFRAC(I)=WFRAC(I)/TOT
      WRITE (18,2036) PROD,(WFRAC(I),I=3,5)
 2036 FORMAT (1X,'PRODUCT RATE ='F7.3,' LB./HR.'/1X,'PRODUCT WEIGHT FRAC
     1TIONS =  AMMONIUM NITRATE ='F7.4/41X,'UREA ='F7.4/
     2  28X,'GUANIDINE NITRATE ='F7.4)
      WCAT=AREA*BULK*TIME
      WRITE(18,2016) WCAT
 2016 FORMAT(1X,'TOTAL CATALYST WEIGHT =',F8.2,' GRAMS')
      RTIME=AREA*TIME/(YO(1)*VOLLIQ)
      WRITE(18,2017) RTIME
 2017 FORMAT(1X,'NOMINAL RESIDENCE TIME =',F7.2, ' MINUTES')
C     WRITE(18,2018)VOLGAS,VOLLIQ
 2018 FORMAT(1X,'MOLAR VOLUME OF GAS ='F9.2,' CU.IN./G.-MOLE'/1X,'MOLAR
     1VOLUME OF LIQUID =',F6.2,' CU.IN./G-MOLE')
C     WRITE(18,2019) H
 2019 FORMAT(1X,'INTEGRATION STEP SIZE =',F5.2)
      WRITE(18,2020) FREQGN,EGN,FREQU,EU
 2020 FORMAT(1X,'RATE CONSTANT FOR GN  '/5X,'FREQUENCY FACTOR ='E12.4/5X
     1,'ACTIVATION ENERGY ='E12.4/1X,'RATE CONSTANT FOR UREA DECOMPOSITI
     1ON'/5X, 'FREQUENCY FACTOR ='E12.4/5X,'ACTIVATION ENERGY ='E12.4)
      RH=R1/5.0
      DO 74 J=1,6
 74   RPRINT(J)=RH*FLOAT(J-1)
      WRITE (18,75)(RPRINT(J),J=1,6)
 75   FORMAT         (1H1,//1X,'DISTANCE',28X,'RADIAL    TEMPERATURE    PRO
     1FILES'/9X, 6(3X,'R ='F7.3,2X)/)
      REWIND NU
      DO 77 I=1,ITAPE
      READ (NU) TIME,(TR2(J),J=1,NN,NREL)
      READ (NU) RI,RELIQ
      SAVE(1,I)=TIME
      SAVE(2,I)=RI
      SAVE(3,I)=RELIQ
      DO 79 J=1,NN,NREL
 79   TR2(J)=TR2(J) - 273.0
 77   WRITE (18,78) TIME,(TR2(J),J=1,NN,NREL)
 78   FORMAT (F9.3,6(F12.3,3X))
      WRITE (18,95)
 95   FORMAT (1H1,16X,'TIME',18X,'RI',15X,'RELIQ'/)
      DO 96 I=1,ITAPE
 96   WRITE (18,97) (SAVE(J,I),J=1,3)
 97   FORMAT (3F20.4)
 82   CONTINUE
      END
```

```
      SUBROUTINE SYST (XY,YY,[illegible])
      REAL MOLGAS,[illegible]
      DIMENSION YY([illegible]),F[illegible]([illegible])
      COMMON [illegible]
     1   HR,[illegible],MOLGAS,[illegible]
      SPGN=FREQGN*EXP(-E[illegible]/(YY(6)))
      SPH=FREQH*EXP(-[illegible]/(YY(6)))
      RGN=SPGN*YY(1)*YY(3)
      RH=-SPH*YY(5)*YY(4)**2
      FUNC(1)=RH*[illegible]*AREA
      FUNC(2)=3.0*[illegible]*AREA
      FUNC(3)=(-RG[illegible]*AREA - YY(3)*F[illegible]([illegible]))/YY(1))
      FUNC(4)=(([illegible]*AREA - YY(4)*F[illegible]([illegible]))/YY(1))
      FUNC(5)=(([illegible]*AREA - YY(5)*F[illegible]([illegible]))/YY([illegible]))
      FUNC(6)=(1.0/((CP*YY(1) + [illegible]*YY(2)))*([illegible])*[illegible])*
     1   (CMI*FUNC(1) +
     2 CMG*FUNC(2)) - HD*[illegible] - [illegible]*(YY([illegible])-[illegible]))
      RETURN
      END
```

```
      SUBROUTINE RUNGE (A,B,C,N,TIME,H,AK,F[illegible],Y[illegible],M)
C
C     ***********************************************************************
C     THIS SUBROUTINE INTEGRATES A SET OF ORDINARY DIFFERENTIAL EQUATIONS
C      OVER ONE STEP BY A GENERALIZED EXPLICIT RUNGE-KUTTA PROCEDURE.
C      THE RUNGE-KUTTA COEFFICIENTS MUST BE PROVIDED AS WELL AS A SUBROUTINE
C      FOR EVALUATING THE SYSTEM EQUATIONS.
C     NO CHANGES SHOULD BE REQUIRED IN THE [illegible].
C     ***********************************************************************
C
C     FOR A SINGLE PRECISION VERSION OF THIS PROGRAM, REMOVE THE FOLLOWING
C        CARDS.
C     IMPLICIT REAL*8 (A-H,O-Z)                                        ******
C
      DIMENSION A(M,M),B(M),C(M),Y(N),AK(N,M),F[illegible](N),YY(N)
C
C
C     NOMENCLATURE
C     M = NUMBER OF FUNCTION EVALUATIONS IN THE RUNGE-KUTTA METHOD.
C     A = ARRAY OF DIMENSION M X M.
C     B = VECTOR OF DIMENSION M.
C     C = VECTOR OF DIMENSION M.
C     N = NUMBER OF SYSTEM EQUATIONS TO BE INTEGRATED.
C     Y = VECTOR OF DIMENSION N OF DEPENDENT VARIABLES.
C     H = INTEGRATION STEP SIZE.
C     TIME = INDEPENDENT VARIABLE.
C
C     GENERALIZED RUNGE-KUTTA REPRESENTATION
C
C          C(1) | A(1,1)  A(1,2)  . . . . .   A(1,M)
C          C(2) | A(2,1)  . . . . . . . . .   A(2,M)
C           .   | . . . . . . . . . . . . . . . . .
C           .   | . . . . . . . . . . . . . . . . .
C           .   | . . . . . . . . . . . . . . . . .
C          C(M) | A(M,1)  . . . . . . . . .   A(M,M)
C          -----|-----------------------------------
C               | B(1)     B(2), . . . . . . .  B(M)
C
C        WHERE,
C             K = H * FUN[illegible]( X + C*H , YI + [illegible] (A*K ) )
C             Y(I) = YI + [illegible](B* )
C
C
C     CALCULATE THE K'S.
      DO 1 IM=1,M
      DO 2 IN=1,N
      DOTPRD=0.0
      IF(IM .EQ. 1) GO TO 2
      III=IM - 1
      DO 1 ICOL=1,III
    1 DOTPRD=A(IM,ICOL)*AK(IN,ICOL) + DOTPRD
    2 YY(IN)=Y(IN) + DOTPRD
```

```
C      EVALUATE THE SYSTEM EQUATIONS.
       XX=TIME + C(IM)*H
       CALL SYST(XX,YY,FUNC,N)
C
       DO 3 IN=1,N
  3    AK(IN,IM)=H * FUNC(IN)
  4    CONTINUE
C
C      CALCULATE THE PRODUCT OF THE KIS AND BIS.
       DO 5 IN=1,N
       DOTPRD=0.0
       DO 6 IM=1,M
  6    DOTPRD=AK(IN,IM) * B(IM)  +  DOTPRD
  5    Y(IN)=Y(IN) + DOTPRD
C
       RETURN
       END
```

```
      SUBROUTINE RADIAL (Y,XY),NP,TR1,T2,RR,N,[illegible])
      REAL MOLGAS,MOLLIQ
      DIMENSION Y(6),XM(6),AA(51),BB(51),CC(51),DD(51),TR1(51),TR2(51)
      DIMENSION XXY(6)
      COMMON FREQG,FREQL,EG,EL,BULK,VOID,TF[illegible],AREA,DIAM,[illegible]TC,PI,
     1    HS,CML,CMG,TO,MOLGAS,PPART,R1,R2,S
      DATA ALPHA,BETA,VISL1,VISG1,RHOL,CP/1.5[illegible],1.75,1.0,0.0,2.1,4.0,.50/
      DO 7 I=1,NN
    7 TR1(I)=TR2(I)
C     BEGIN EQUATIONS
      VISL=VISL1*2.54*0.6
      VISG=VISG1*2.54*0.6
      RHOG=25.0/(MOLGAS*16.4)
      GLIQ=Y(1)*(Y(3)*XM(3)+Y(4)*XM(4)+Y(5)*XM(5))/AREA
      GGAS=Y(2)*26.0/AREA
      RELIQ=PPART*GLIQ/(VISL*(1.0-VOID))
      REGAS=PPART*GGAS/(VISG*(1.0-VOID))
      DELLIQ=RELIQ*(ALPHA+BETA*RELIQ)*RHOG*VISL**2
      DELGAS=REGAS*(ALPHA+BETA*REGAS)*RHOL*VISG**2
C     LARKIN CORRELATION
      IF (DELGAS .LE. 1.0E-05) GO TO 20
      CHI=SQRT(DELLIQ/DELGAS)
      IF(CHI.LE.30.0) GO TO 6
   20 RL=1.0
      GO TO 5
    6 RL=-.774+0.525*ALOG10(CHI)-0.109*(ALOG10(CHI))**2
      RL=10.0**RL
    5 CONTINUE
C     WEEKMAN
      RELIQ=DIAG*GLIQ/(VISL*VOID*RL)
      COND=1.0
      VISL=VISL1*2.42
      PRANDL=CP*VISL/COND
      EFFK=7.03*2.85E-04*RELIQ[illegible]*PRANDL
      EFFK=EFFK*1.13E-03*2.[illegible]*60.0
C     TRIDIAGONAL SYSTEM
      SCON=FREQG*EXP(-EG/Y(6))
      SCOL=FREQL*EXP(-EL/Y(6))
      RG =SCON*Y(4)*Y(3)
      RL=-SCOL*Y(3)*Y(4)**2
      F1=RG*BULK
      F2=3.0*RG*BULK
      PHI=(CML*Y(1)+CMG*Y(2))/AREA
      PSI=CML*F1+CMG*F2
      GHS=HR*RGM*BULK-PSI*TO
      DR=R1/FLOAT(NN-1)
      NT=NN-1
      DO 10 I=2,NT
      RAD=DR*FLOAT(I-1)
      CC(I)=EFFK/(2.0*DR**2)+EFFK/(4.0*DR*RAD)
      BB(I)=-EFFK/DR**2-PHI/DR-PSI/2.0
      AA(I-1)=EFFK/(2.0*DR**2)-EFFK/(4.0*DR*RAD)
      C=CC(I)
```

```
      B=-EFFK/(PH**2)+PHI/PK-PSI/2.0
      A=AA(J-1)
   10 DD(J)=-TR1(J+1)*C-TR1(J)*B-TR1(J-1)*A+RHS
      BB(1)=-2.0*EFFK/PH**2-PHI/PK-PSI/2.0
      CC(1)=2.0*EFFK/PH**2
      C=CC(1)
      B=-2.0*EFFK/PH**2+PHI/PK-PSI/2.0
      DD(1)=-TR1(2)*C-TR1(1)*B+RHS
      RAD=PH*FLOAT(NN-1)
      RLNM=(R2-R1)/ALOG(R2/R1)
      TERM=2.0*PH*US*RLNM/(EFFK*RAD)
      BB(NN)=-EFFK/PH**2-PHI/PK-PSI/2.0-2.0*TERM*(EFFK/(2.0*PH**2)
     1+EFFK/(4.0*PH*RAD))
      AA(NN-1)=EFFK/PH**2
      DD(NN)=-TR1(NN)*(-EFFK/PH**2+PHI/PK-PSI/2.0)
     1   -TR1(NN-1)*(EFFK/PH**2) + RHS
     2-2.0*TERM*TC*(EFFK/(2.0*PH**2) + EFFK/(4.0*PH*RAD))
      CALL TRIDAG(AA,BB,CC,DD,NN)
      DO 11 J=1,NN
   11 TR2(J)=DD(J)
      SUM=0.0
      DO 15 J=2,NN
      TAV=(TR2(J)+TR2(J-1))/2.0
      RAD1=PH*FLOAT(J-2)
      RAD2=PH*FLOAT(J-1)
   15 SUM=SUM+TAV*PI*(RAD2**2-RAD1**2)
      XXX(6)=SUM/(PI*RAD2**2)
      RETURN
      END
```

```
      SUBROUTINE TRIDAG (A,B,C,D,N)
      DIMENSION A(N),B(N),C(N),D(N)
      D(1)=D(1)/B(1)
      W=B(1)
      DO 1 J=2,N
      B(J-1)=C(J-1)/W
      W=B(J) - A(J-1)*B(J-1)
1     D(J)=(D(J) - A(J-1)*D(J-1))/W
      M=N - 1
      DO 2 J=1,M
      ISUB=N - J
2     D(ISUB)=D(ISUB) - B(ISUB)*D(ISUB+1)
      RETURN
      END
      EOF
```

APPENDIX I-3

CONTINUOUS STIRRED TANK MODEL

A detailed description of the continuous stirred tank model is presented in this section. The method of solution of the discrete difference equations is also given.

Model Development

Consider the series of stirred tanks depicted in Figure B-1. The material balances for guanidine nitrate, urea, and ammonium nitrate can be written for the nth tank:

$$(1) \quad F^{(n)} Y_{GN}^{(n)} - F^{(n-1)} Y_{GN}^{(n-1)} = R_{GN}^{(n)} \cdot W_c^{(n)}$$

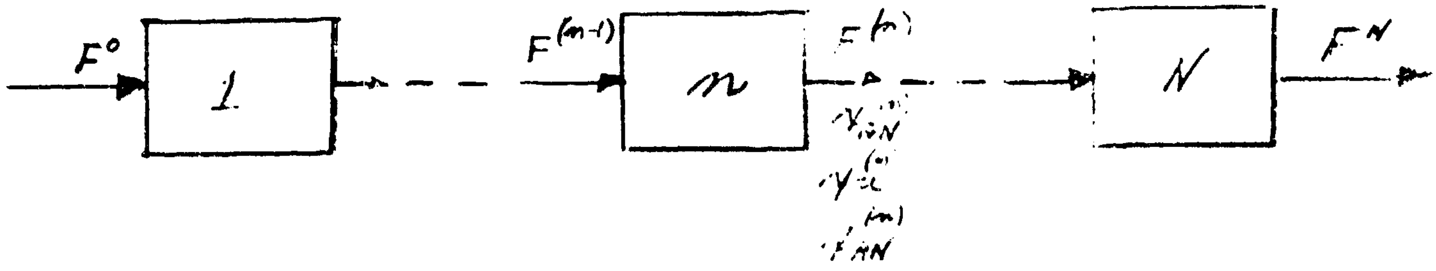
$$(2) \quad F^{(n)} Y_{U}^{(n)} - F^{(n-1)} Y_{U}^{(n-1)} = R_{U}^{(n)} \cdot W_c^{(n)}$$

$$(3) \quad F^{(n)} Y_{AN}^{(n)} - F^{(n-1)} Y_{AN}^{(n-1)} = R_{AN}^{(n)} \cdot W_c^{(n)}$$

The notation is defined at the end of this section. Notice that both sides of each equation have been divided by the molar feed rate to the first vessel, F^{o}, so that the factors $F^{(n)}$, $F^{(n-1)}$, and $W_c^{(n)}$ are all expressed on the same basis of one mole/minute of feed to the first reactor. The rate expressions are given by:

FIGURE B-1

CASCADE OF N STIRRED TANKS



$W_C^{(n)}$-grams of catalyst in reactor n.

$$(4) \qquad R_{GN}^{(n)} = x_{U}^{(n)} \cdot x_{AN}^{(n)} \cdot k_{GN}^{\circ} \, e^{-E_{GN}/R \cdot T^{(n)}}$$

$$(5) \qquad R_{U}^{(n)} = -x_{U}^{(n)2} \cdot x_{AN} \cdot k_{U}^{\circ} \, e^{-E_{U}/R\,T^{(n)}}$$

$$(6) \qquad R_{AN}^{(n)} = -R_{GN}^{(n)}$$

By summing Equations (1), (2), and (3), the following equation relating the flow rates results:

$$(7) \qquad F^{(n)} = F^{(n-1)} + R_{U}^{(n)} \cdot W_{c}^{(n)}$$

Equations (1) through (7) are solved simultaneously for each tank in sequence.

Numerical Solution

If Equations (5) and (7) are substituted into Equation (2), the following cubic equation results:

$$(8)\quad \left(x_u^{(n)}\right)^3 - \left(x_u^{(n)}\right)^2 - M x_u^{(n)} + M x_u^{(n-1)} = 0$$

where

$$M = \frac{F^{(n-1)}}{k_c^{(n)} \cdot k_{cu} \cdot x_{AN}^{(n)}}$$

$$k_{cu}^{(n)} = k_{cu}^{o}\, e^{-E_u/RT^{(n)}}.$$

All terms with superscript (n-1) are known and those terms with superscript (n) are unknown. Therefore, before Equation (8) can be solved for $x_u^{(n)}$, an Equation for $x_{AN}^{(n)}$ must be provided in order that M can be specified. By substituting Equations (6) and (4) into Equation (3), the following quadratic expression results:

$$(9)\quad \left(x_{AN}^{(n)}\right)^2 - N x_{AN}^{(n)} + P x_{AN}^{(n-1)} = 0$$

where

$$N = \frac{w_c^{(n)} \cdot k_{cAN}^{(n)} \cdot x_u^{(n)} + F^{n-1}}{w_c^{(n)} k_{cu}^{(n)} (x_u^{(n)})^2}$$

$$P = \frac{F^{n-1}}{w_c^{(n)} \cdot k_{cu}^{(n)} (x_u^{(n)})^2}$$

$$k_{cAN} = k_{cAN}^{\circ} e^{-E_{cAN}/RT^{n}}$$

Equations (8) and (9) are simultaneous functions of the unknown $x_{AN}^{(n)}$ and $x_u^{(n)}$. These equations for the nth reactor were solved by the following iterative algorithm:

1. Assume a value for x_{AN}^{n}. A convenient first assumption is $x_{AN}^{n} = x_{AN}^{(n-1)}$
2. Solve the cubic equation, Equation (8), for $x_u^{(n)}$
3. Using this value for $x_u^{(n)}$, solve the quadratic equation, Equation (9), for $x_{AN}^{(n)}$

4. Check whether this value of $x_{AN}^{(n)}$ is equal to that assumed in step 1. If it is, the solution for $x_{AN}^{(n)}$ and $x_u^{(n)}$ for the nth reactor is complete. If not, repeat this procedure from step 2 using this newly generated value of $x_{AN}^{(n)}$.

Using this procedure, no convergence difficulties were encountered for any of the cases treated. A listing of the computer program for solving the stirred tank model is included in Appendix I-4.

SYMBOLS FOR STIRRED TANK REACTOR MODEL

E_i = activation energy for component i.

$F^{(n)}$ = molar flow rate of stream (n) per mole/minute of feed

k_i^o = specific rate constant for the formation of component i, moles/(gram of catalyst)-(minute)

$R_j^{(n)}$ = rate of formation of component i in reactor (n); moles/(gram of catalyst)-(minute)

$W_c^{(n)}$ = weight of catalyst in reactor (n)

$x_i^{(n)}$ = mole fraction of component i in stream (n).

APPENDIX I-4. LISTING OF PROGRAM

CONTINUOUS STIRRED TANK REACTOR MODEL

```
C      CONTINUOUS STIRRED TANK REACTOR MODEL ----, 1, [illegible]
       DIMENSION COMENT(60),CAT(5),TEMP(5),[illegible]( ), CAT( ),[illegible](5),[illegible](5),
      1XMO(5),XTF(5),YFEED(5),X2TF(5),VOL(5),YY(5)
       RCTLIQ=0.75
       RCTCOV=0.5
       READ(9,1)NTANKS
       READ(9,3)(WCAT(I),I=1,NTANKS)
       READ(9,1,END=999) NCARDS
       NC=20*NCARDS
       READ(9,2)(COMENT(I),I=1,NC)
       READ(9,2000)(CAT(I),I=1,5),BULK,PORSTY
       READ(9,3)(TEMP(I),I=1,NTANKS)
       READ(9,2010)[illegible],F[illegible],FEEDH,F[illegible]
   995 READ(9,3,END=999) (XO(I),I=1,3),FEED
     1 FORMAT(8I10)
     2 FORMAT(20A4)
     3 FORMAT(4F20.10)
  2000 FORMAT(5A4,3F10.5)
  2010 FORMAT(4F20.10)
       DO 5 I=1,NTANKS
     5 VOL(I)=WCAT(I)*2.[illegible]/(BULK*1728.0)
       XM(1)=50.0
       XM(2)=60.0
       XM(3)=122.0
       TOTAL=0.0
       DO 6 I=1,3
     6 TOTAL=TOTAL+YO(I)*XM(I)
       DO 7 I=1,3
     7 YO(I)=YO(I)*XM(I)/TOTAL
       FEEDW=FEEDM*TOTAL*(60.0/453.6)
       YO(4)=FEEDM
       XO(4)=FEEDW
       WRITE(18,31)(COMENT(I),I=1,NC)
    31 FORMAT(1H1,(2X,(20A4)))
       WRITE(18,2011)(CAT(I),I=1,5),BULK,PORSTY
  2011 FORMAT(/1X,5A4/3X,'BULK DENSITY =',F6.2,' [illegible]',1[illegible],'/3X,'[illegible]
      1 POROSITY =',F6.2,' VOL.VOL.')
       WRITE (18,5010)
  5010 FORMAT(                  '1',' NOTE = CATALYST [illegible]
      1E, AND PRODUCT FLOW RATES ARE GIVEN'/3X,'RATIO [illegible] TO THE [illegible]
      2 FEED RATE TO THE FIRST REACTOR.')
       DO 8 I=1,4
     8 YFEED(I)=XO(I)
       DO 50 K=1,NTANKS
       VCAT=WCAT(K)*7.48/(BULK*1728.0)
       VOLGAL=VOL(K)*7.48
       WRITE(18,5000)K,WCAT(K),VCAT,TEMP(K),VOL(K),VOLGAL
  5000 FORMAT (//1X,'REACTOR',I2,5X,'CATALYST =',F[illegible].2,' [illegible]',
      1 F9.4,' GAL.'/18X,'TEMPERATURE =',F5.1,' [illegible].'/18X,
      2 'NOMINAL VOLUME =',F9.4,' CU. FT.',',F[illegible].4,' GAL.'/)
       WRITE(18,5011) XO(4),(YO(I),I=1,4)
  5011 FORMAT(10X,'INLET FEED RATE =',F7.4,' [illegible]/[illegible]',/X,
      1' MOLE FRACTIONS'/6X,'[illegible] =',F7.[illegible],' [illegible] =',F7.4/
```

```
     252X,'GUANIDINE NITRATE ='F7.4)
      WRITE(18,5002)   XO(4),(XO(I),I=1,3)
 5002 FORMAT(/10X,'INLET FEED RATE ='F7.4,' MOLES/MINUTE',11X,
     1'MOLE FRACTIONS'/53X,'AMMONIUM NITRATE ='F7.4/65X,'UREA ='F7.4/
     252X,'GUANIDINE NITRATE ='F7.4)
      SPGN=FREQGN*EXP(-EGN/(TEMP(K)+273.0))
      SPU=FREQU*EXP(-EU/(TEMP(K)+273.0))
      ICOUNT=0
      XU=-1.0
      XAN=XO(1)
   53 ICOUNT=ICOUNT+1
      A=1.0
      B=-1.0
      C=-XO(4)/(WCAT(K)*SPU*XAN)
      D=-C*XO(2)
      CALL CUBIC(A,B,C,D,XX,XTF(2),ITYPE,NREAL)
      A=0.0
      B=WCAT(K)*SPU*XTF(2)**2
      C=-WCAT(K)*SPGN*XTF(2)-XO(4)
      D=XO(4)*XO(1)
      CALL CUBIC(A,B,C,D,XX,XTF(1),ITYPE,NREAL)
      IF(ABS((XTF(1)-XAN)/XAN).GT.1.0E-05) GO TO 51
      IF(ABS((XTF(2)-XU)/XU).GT.1.0E-05) GO TO 51
      GO TO 52
   51 XU=XTF(2)
      XAN=XYF(1)
      IF(ICOUNT.LT.50) GO TO 53
      WRITE(18,54)XU,XTF(2),XAN,XTF(1)
   54 FORMAT(///'ITERATION IS NOT CONVERGE '4F12.4)
      CALL EXIT
   52 XTF(4)=XO(4)-WCAT(K)*SPU*XTF(1)*XTF(2)**2
      XTF(3)=(1.0/XTF(4))*(XO(4)*XO(3)+WCAT(K)*SPGN*XTF(1)*XTF(2))
      CONV=(XTF(2)*XTF(4)-XFEED(2)*XFEED(4))/(XFEED(2)*XFEED(4))
      CONV=-CONV
      YIELD=(XTF(3)*XTF(4)-XFEED(3)*XFEED(4))/
     1    (XTF(2)*XTF(4)-XFEED(2)*XFEED(4))
      YIELD=-YIELD
      GAS=3.0*WCAT(K)*SPGN*XTF(1)*XTF(2)
      TOTAL=0.0
      DO 9 I=1,3
    9 TOTAL=TOTAL+XTF(I)*WM(I)
      DO 10 I=1,3
   10 XWTF(I)=XTF(I)*WM(I)/TOTAL
      XWTF(4)=XTF(4)*(60.0/453.6)*TOTAL
      WRITE(18,5003)XWTF(4),(XWTF(I),I=1,3)
 5003 FORMAT(/10X,'PRODUCT FLOW RATE ='F7.4,' LB./HR.',14X,
     1'WEIGHT FRACTIONS'/53X,'AMMONIUM NITRATE ='F7.4/65X,'UREA ='F7.4/
     252X,'GUANIDINE NITRATE ='F7.4)
      WRITE(18,5004)XTF(4),(XTF(I),I=1,3)
 5004 FORMAT(/10X,'PRODUCT FLOW RATE ='F7.4,' MOLES/MINUTE',11X,
     1'MOLE FRACTIONS'/53X,'AMMONIUM NITRATE ='F7.4/65X,'UREA ='F7.4/
     252X,'GUANIDINE NITRATE ='F7.4)
      WRITE(18,5005) GAS
```

```
5005 FORMAT(10X,'GAS FLOW RATE ='F7.4,' MOLES/MINUTE')
      WRITE(18,5006) CONV,YIELD
5006 FORMAT(10X,'TOTAL CONVERSION ='F7.4,' MOLES UREA REACTED/MOLE UREA
     1 FED'/10X,'TOTAL YIELD ='F7.4,' MOLES GN/MOLE UREA REACTED')
      WRITE(18,2020) FREQG,EGN,FREQU,EU
2020 FORMAT(10X,'RATE CONSTANT FOR GN'/15X,'FREQUENCY FACTOR ='F12.4/
     115X,'ACTIVATION ENERGY ='F12.4/10X,'RATE CONSTANT FOR UREA DECOMPO
     2SITION'/15X,'FREQUENCY FACTOR ='F12.4/15X,'ACTIVATION ENERGY =',
     3 F12.4)
      DO 11 I=1,4
      X20(I)=X2TE(I)
 11   X0(I)=XTE(I)
      WRITE(18,51)(CONENT(I),I=1,NC)
  50 CONTINUE
      GO TO 908
 999 CALL EXIT
      END
```

```
      SUBROUTINE CUBIC(A,B,C,D,XX,XREAL,ITYPE,NREAL)
C     SOLUTION OF CUBIC AND QUADRATIC EQUATIONS.
      DIMENSION XX(3),IROUND(3)
      CUBRT(ARG)=SIGN(ABS(ARG)**(1.0/3.0),ARG)
      DO 500 I=1,3
  500 IROUND(I)=0
      IF(A)200,110,200
  110 IF(B)140,120,140
  120 IF(C)130,999,130
  130 X=-D/C
      XX(1)=X
      ITYPE=1
      GO TO 100
  140 P=-C/(B+B)
      Q=-D/B
      R=P*P+Q
      IF(R)160,150,150
  150 X=SIGN(ABS(P) + SQRT(R),P)
      Y=-Q/X
      XX(1)=X
      XX(2)=Y
      ITYPE=2
      GO TO 100
  160 Y=SQRT(-R)
      XX(1)=0.0
      XX(2)=P
      XX(3)=Y
      ITYPE=3
      GO TO 100
  200 IF(D)300,210,300
  210 X3=0.0
      IF(C)230,220,230
  220 X2=0.0
      X1=-B/A
      GO TO 330
  230 P=-B/(A+A)
      Q=-C/A
      R=P*P+Q
      IF(R)250,240,240
  240 X1=P+SQRT(R)
      X2=P+P-X1
      GO TO 330
  250 Y=SQRT(-R)
      GO TO 350
  300 P=B/(3.0*A)
      Q=C/(3.0*A)
      R=D/A
      ALPHA=Q-P*P
      BETA=ALPHA*P+0.5*(P*Q-R)
      GAMMA=ALPHA*ALPHA*ALPHA+BETA*BETA
      IF (GAMMA.GT.1.E-5) GO TO 340
      IF(GAMMA.GT.-1.E-5) GO TO 320
  310 SQT=SQRT(-GAMMA)
```

```
      PHI=ATAN2(SQT,BETA)/3.0
      Q=2.0*SQRT(-ALPHA)
      Y1=Q*COS(PHI)-P
      THPI=2.0*3.1416/3.0
      THPI2=2.0*THPI
      Y2=Q*COS(PHI+THPI)-P
      Y3=Q*COS(PHI+THPI2)-P
      GO TO 330
  320 CUBE=-SQRT(-ALPHA)
      Y1=-CUBE-CUBE-P
      Y2=CUBE-P
      Y3=Y2
  330 YY(1)=Y1
      YY(2)=Y2
      YY(3)=Y3
      ITYPE=4
      GO TO 100
  340 SQT=SQRT(GAMMA)
      E=CUBRT(BETA+SQT)
      F=CUBRT(BETA-SQT)
      Y3=E+F-P
      R=-0.5*(E+F)-P
      Y=0.866*(E-F)
  350 YY(1)=Y3
      YY(2)=R
      YY(3)=Y
      ITYPE=5
      GO TO 100
  999 CONTINUE
      RETURN
    1 FORMAT(4F20.0)
    2 FORMAT(8X,'A',10X,'B',10X,'C',10X,'D',11X,'R1',9X,'R2',9X,'R3')
    5 FORMAT(22X,3F11.5,10X,'LINEAR EQUATION')
    6 FORMAT(11X,5F11.5,'TWO REAL ROOTS')
    7 FORMAT(11X,3F11.5,11X,2F11.5,' *')
    8 FORMAT(7F11.5)
    9 FORMAT(7F11.5,' *')
   15 FORMAT (1H1)
  996 FORMAT(/5X'* INDICATES R2 IS REAL PART AND R3 IS IMAGINARY PART OF
     1 COMPLEX PAIR'//)
  100 CONTINUE
      IF(ITYPE .EQ. 1 .OR. ITYPE .EQ. 5) NREAL=1
      IF(ITYPE .EQ.3) NREAL=0
      IF(ITYPE .EQ. 2) NREAL=2
      IF (ITYPE .EQ. 4) NREAL=3
      DO 501 I=1,NREAL
  501 IF(YY(I) .GE. 0.0 .AND. YY(I) .LE. 1.0) IFOUND(I)=1
      ICOUNT=0
      DO 502 I=1,NREAL
  502 IF(IFOUND(I) .EQ. 1) ICOUNT=ICOUNT+1
      IF (ICOUNT .NE. 0) GO TO 503
      WRITE (16,504)
  504 FORMAT (//,'NO ROOT BETWEEN 0 AND 1')
```

```
      CALL EXIT
  503 GO TO (601,602,603),ICOUNT
  601 DO 505 I=1,NREAL
      IF (IROUND(I) .NE. 1) GO TO 505
      XREAL=XX(I)
  505 CONTINUE
      RETURN
  602 WRITE (18,506) (XX(I),I=1,3)
  506 FORMAT (//,'TWO REAL ROOTS BETWEEN 0 AND 1',3E12.4)
      CALL EXIT
  603 WRITE (18,507) (XX(I),I=1,3)
  507 FORMAT (//,'THREE REAL ROOTS BETWEEN 0 AND 1',3E12.4)
      CALL EXIT
      END
      EOF
```

APPENDIX I-5. COST STUDIES

COST STUDY - GUANIDINE NITRATE
CASE NO.101

Basis: Basic Case
Cont. Process; 1 hr. reaction
AN/U/Cat. = 2/2/1.7
U Yld. = 80%; U Conv. = 64.5%
AN Yld. = 100%; AN Conv. = 32%

*PRODUCTION COSTS

PLANT CAPACITY 80.0 MM LBS/YR

	UNITS	RATE/UNIT	CENTS/LB	** SENSITIVITY PCT CHANGE	Gov't Acctg
INVESTMENT (MM $)					
BATTERY LIMIT			6.42		6.42
OFFSITE AND ALLOCATED AUX.			1.20		1.20
TOTAL (MM $)			7.62	11	7.62
PROCESSING COST (CENTS/LB)					
DEPRECIATION		10.0 PCT INV	.95(1)		-
M AND RL		5.0 PCT INVEST	.48		.24
OPERATING LABOR	16.00 MEN	8600.0 $/MAN-YR	.17	[illegible]	.17
CHEMICAL CONTROL	4.00 MEN	10000.0 $/MAN-YR	.05	[illegible]	.05
SUPERVISION	4.00 MEN	12000.0 $/MAN-YR	.06	[illegible]	.05
ELECTRICITY	.20 KWH/LB	1.0 CNTS/KWH	.20	[illegible]	.20
STEAM	4.00 LB /LB	75.0 CNTS/M LB	.30	[illegible]	.30
WATER	10.00 GAL/LB	10.0 CNTS/M GAL	.10	[illegible]	.10
FUEL	.01 GAL/LB	7.0 CNTS/GAL	.10	[illegible]	.10
TOTAL (CENTS/LB)			[illegible]		1.22
RAW MATERIAL COST (CENTS/LB)					
UREA	1.23200 LB/LB	4.00 CNTS/LB	4.93	[illegible]	4.93
AMMONIUM NITRATE	.65600 LB/LB	[illegible] CNTS/LB	1.64	[illegible]	1.64
CATALYST	.00100 LB/LB	150.00 CNTS/LB	.15	[illegible]	.15
TOTAL (CENTS/LB)			6.72		6.72
PLANT OVERHEAD (CENTS/LB)			.18		.18
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDIT			9.31		8.12
BY-PRODUCT CREDIT (CENTS/LB)					
AMMONIUM CARBAMATE	.60000 LB/LB	.00 CNTS/LB	.00		.000
TOTAL (CENTS/LB)			.00		.00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT			9.31		8.12
				Fringe	1.69
				Price 0% Return	9.81¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT

** PERCENT CHANGE NEEDED TO AFFECT RETURN BY 5 PERCENTAGE POINTS

(1) 50% is maintenance material

RETURN CALCULATIONS

PLANT INVEST $ 7.6 MM
WORK CAPITAL $.[illegible] MM
[illegible] $ 1.[illegible] MM
TOTAL [illegible] $ [illegible] MM

PRICE FOR 10 PCT RETURN 11.[illegible] CENTS/LB
PRICE FOR 20 PCT RETURN 1[illegible] CENTS/LB
PRICE FOR 30 PCT RETURN 1[illegible] CENTS/LB

COST STUDY - GUANIDINE NITRATE
CASE NO.102

Basis: Cont. Process; 1 hr. reaction
AN/U/Cat. = 2/2/1.7
U Yld. = 80%; U Conv. = 64.5%
AN Yld. = 100%; AN Conv. = 32%

*PRODUCTION COSTS

PLANT CAPACITY 20.0 MM LB/YR

	UNITS	RATE/UNIT	**SENSITIVITY LIKELY	PCT CHANGE	Gov't Acctg
INVESTMENT (MM $)					
BATTERY LIMIT			2.78		2.78
OFFSITE AND ALLOCATED AUX.			.90		.90
TOTAL (MM $)			3.68	10	3.68
PROCESSING COST (CENTS/LB)					
DEPRECIATION		10.0 PCT INVST	1.84		-
MM AND RL		5.0 PCT INVST	.92(1)		.46
OPERATING LABOR	12.00 MEN	8600.0 $/MAN-YR	.52	126	.52
CHEMICAL CONTROL	4.00 MEN	10000.0 $/MAN-YR	.20	325	.20
SUPERVISION	4.00 MEN	12000.0 $/MAN-YR	.24	270	.24
ELECTRICITY	.20 KWH/LB	1.0 CNT/KWH	.20	406	.20
STEAM	4.00 LB /LB	75.0 CNT/M LB	.30	270	.30
WATER	10.00 GAL/LB	10.0 CNT/MGAL	.10	811	.10
FUEL	.01 GAL/LB	7.0 CNT/ GAL	.10	773	.10
TOTAL (CENTS/LB)			4.42		2.12
RAW MATERIAL COST (CENTS/LB)					
UREA	1.23200 LB/LB	4.00 CNT/LB	4.93	16	4.93
AMMONIUM NITRATE	.65600 LB/LB	2.50 CNT/LB	1.64	48	1.64
CATALYST	.00100 LB/LB	150.00 CNT/LB	.15	530	.15
TOTAL (CENTS/LB)			6.72		6.72
PLANT OVERHEAD (CENTS/LB)			.45		.45
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS			11.58		9.29
BY-PRODUCT CREDIT (CENTS/LB)					
AMMONIUM CARBAMATE	.60100 LB/LB	.00 CNT/LB	.00		.00
TOTAL (CENTS/LB)			.00		.00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS			11.58		9.29
				fringe	2.02

Price 0% Return 11.31¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT

** PERCENT CHANGE NEEDED TO AFFECT RETURN BY 2 PERCENTAGE POINTS

(1) 50% is maintenance material

RETURN CALCULATION

PLANT INVEST	$	3.7 MM
CORP ALLOC	$	.1 MM
WORKING CAP	$	.4 MM
TOT OP ASSETS	$	4.1 MM

PRICE FOR 0 PCT RETURN 12.6 CENTS/LB
PRICE FOR 20 PCT RETURN 18.6 CENTS/LB
PRICE FOR 30 PCT RETURN 21.2 CENTS/LB

COST STUDY - GUANIDINE NITRATE
[illegible] NO.210

Basis: Cont. Process; 2 hr. reaction
AN/U/Cat. = 2/2/1.7
U Yld. = 87%; U Conv. = 88%
Yld. on AN = 100%

PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

	UNITS		RATE/UNIT		CENTS/LB	**SENSITIVITY PCT CHANGE	Gov't Acctg
INVESTMENT (MM $)							
BATTERY LIMIT					[illegible]		4.84
OFFSITE AND ALLOCATED AUX.					1.00		1.00
TOTAL (MM $)					[illegible]	11	5.84
PROCESSING COST (CENTS/LB)							
DEPRECIATION			10.0	PCT INVEST	1.46		-
MM AND RL			5.0	PCT INVEST	.73(1)		.37
OPERATING LABOR	12.00	MEN	8600.0	$/MAN-YR	.26	[illegible]	.26
CHEMICAL CONTROL	4.00	MEN	10000.0	$/MAN-YR	.10	500	.10
SUPERVISION	4.00	MEN	10000.0	$/MAN-YR	.12	[illegible]	.12
ELECTRICITY	.20	KWH/LB	1.0	CNT/KWH	.20	305	.20
STEAM	4.00	LB /LB	75.0	CNT/M LB	.30	217	.30
WATER	10.00	GAL/LB	10.0	CNT/M GAL	.10	651	.10
FUEL	.01	GAL/LB	7.0	CNT/ GAL	.10	[illegible]	.10
TOTAL (CENTS/LB)					[illegible]		1.55
RAW MATERIAL COST (CENTS/LB)							
UREA	1.13200	LB/LB	4.00	CNT/LB	[illegible]	14	4.53
AMMONIUM NITRATE	.65600	LB/LB	2.50	CNT/LB	1.64	[illegible]	1.64
CATALYST	.00200	LB/LB	150.00	CNT/LB	.30	[illegible]	.30
TOTAL (CENTS/LB)					[illegible]		6.47
PLANT OVERHEAD (CENTS/LB)					[illegible]		.28
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS					[illegible]		8.30
BY-PRODUCT CREDIT (CENTS/LB)							
AMMONIUM CARBAMATE	.60000	LB/LB	.00	CNT/LB	[illegible]		.00
TOTAL (CENTS/LB)					[illegible]		.00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS					[illegible]		8.30
						Fringe	1.78
						Price 0% return	10.08¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT

** PERCENT CHANGE NEEDED TO AFFECT [illegible]

(1) 50% is maintenance material

RETURN CALCULATIONS

PLANT INVEST [illegible]
[illegible]
[illegible]
TOT [illegible]

PRICE FOR [illegible] PCT RETURN [illegible] CNT/LB
PRICE FOR 20 PCT RETURN [illegible] CNTS/LB
PRICE FOR 30 PCT RETURN [illegible] CNTS/LB

COST STUDY - GUANIDINE NITRATE
CASE NO.220

Basis: Cont. Process; 3 hr. reaction
AN/U/Cat. = 2/2/1.7
U Yld. = 88%; U Conv. = 98%
Yld. on AN = 100%

*PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

	UNITS	RATE/UNIT	LIKELY	**SENSITIVITY PCT CHANGE	Gov't Acctg
INVESTMENT (MM $)					
BATTERY LIMIT			5.61		5.61
OFFSITE AND ALLOCATED AUX.			1.00		1.00
TOTAL (MM $)			6.61	10	6.61
PROCESSING COST (CENTS/LB)					
DEPRECIATION		10.0 PCT INVST	1.65		-
MM AND RL		5.0 PCT INVST	.83		.42
OPERATING LABOR	12.00 MEN	8600.0 $/MAN-YR	.26	227	.26
CHEMICAL CONTROL	4.00 MEN	10000.0 $/MAN-YR	.10	585	.10
SUPERVISION	4.00 MEN	12000.0 $/MAN-YR	.12	487	.12
ELECTRICITY	.20 KWH/LB	1.0 CNT/KWH	.20	365	.20
STEAM	4.00 LB /LB	75.0 CNT/M LB	.30	244	.30
WATER	10.00 GAL/LB	10.0 CNT/M GAL	.10	731	.10
FUEL	.01 GAL/LB	7.0 CNT/ GAL	.10	696	.10
TOTAL (CENTS/LB)			3.66		6.56
RAW MATERIAL COST (CENTS/LB)					
UREA	1.11800 LB/LB	4.00 CNT/LB	4.47	16	4.47
AMMONIUM NITRATE	.65600 LB/LB	2.50 CNT/LB	1.64	44	1.64
CATALYST	.00300 LB/LB	150.00 CNT/LB	.45	159	.45
TOTAL (CENTS/LB)			6.56		6.56
PLANT OVERHEAD (CENTS/LB)			.31		.31
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS			10.53		8.47
BY-PRODUCT CREDIT (CENTS/LB)					
AMMONIUM CARBAMATE	.60000 LB/LB	.00 CNT/LB	.00		.00
TOTAL (CENTS/LB)			.00		.00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS			10.53		8.47
				Fringe	1.87
				Price 0% return	10.34¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT

** PERCENT CHANGE NEEDED TO AFFECT RETURN BY 2 PERCENTAGE POINTS

(1) 50% is maintenance material.

RETURN CALCULATIONS

PLANT INVEST $ 6.6 MM
CORP ALLOC $.[illegible] MM
WORKING CAP $ .7 MM
TOT OP ASSETS $ 7.5 MM

PRICE FOR 0 PCT RETURN 1[illegible].[illegible] CENTS/LB
PRICE FOR 20 PCT RETURN 16.[illegible] CENTS/LB
PRICE FOR 30 PCT RETURN 17.[illegible] CENTS/LB

COST STUDY - GUANIDINE NITRATE
CASE NO.301

Basis: Cont. Process; 1 hr. reaction
AN/U/Cat. = 2/2/1.7
U Yld. = 80%; U Conv. = 64.5%
Aqueous Workup

*PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

	UNITS	RATE/UNIT	[illegible]	SENSITIVITY PCT CHANGE**	Gov't Acctg
INVESTMENT (MM $)					
BATTERY LIMIT			[illegible]		3.69
OFFSITE AND ALLOCATED AUX.			[illegible]		.90
TOTAL (MM $)			[illegible]	11	4.59
PROCESSING COST (CENTS/LB)					
DEPRECIATION		10.0 PCT INVEST	1.15		-
MM AND PL		5.0 PCT INVEST	.57 (1)		.29
OPERATING LABOR	10.00 MEN	8600.0 $/MAN-YR	.21	192	.21
CHEMICAL CONTROL	4.00 MEN	10000.0 $/MAN-YR	.10	418	.10
SUPERVISION	4.00 MEN	12000.0 $/MAN-YR	.12	[illegible]	.12
ELECTRICITY	.10 KWH/LB	1.0 CNT/KWH	.10	593	.10
STEAM	5.00 LB /LB	75.0 CNT/M LB	.37	133	.37
WATER	8.00 GAL/LB	10.0 CNT/M GAL	.08	655	.08
FUEL	.01 GAL/LB	7.0 CNT/ GAL	.10	[illegible]	.10
TOTAL (CENTS/LB)			[illegible]		1.37
RAW MATERIAL COST (CENTS/LB)					
UREA	1.23200 LB/LB	4.00 CNT/LB	[illegible]	11	4.93
AMMONIUM NITRATE	.65600 LB/LB	2.50 CNT/LB	[illegible]	31	1.64
CATALYST	.00100 LB/LB	150.00 CNT/LB	.15	341	.15
TOTAL (CENTS/LB)			[illegible]		6.72
PLANT OVERHEAD (CENTS/LB)			[illegible]		.24
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDIT			[illegible]		8.33
BY-PRODUCT CREDIT (CENTS/LB)					
AMMONIUM CARBAMATE	.60000 LB/LB	.00 CNT/LB	.00		.00
TOTAL (CENTS/LB)			[illegible]		.00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT			[illegible]		8.33
				Fringe	1.73
				Price 0% return	10.06¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT

** PERCENT CHANGE NEEDED TO AFFECT RETURN BY [illegible]

(1) 50% is maintenance material

RETURN CALCULATION

PLANT INVEST $ [illegible]
CORP ALLOC $ [illegible]
WORKING CAP $ [illegible]
TOT OP ASSETS $ [illegible]

PRICE FOR 0 PCT RETURN 11.[illegible] CNTS/LB
PRICE FOR 20 PCT RETURN [illegible] CNTS/LB
PRICE FOR 30 PCT RETURN [illegible] CNTS/LB

COST STUDY - GUANIDINE NITRATE
CASE NO.501

Basis: Cont. Process; 1 hr. reaction
AN/U/Cat. = 2/2/1.7
U Yld. = 80%; U Conv. = 64.5%
Agitating reactor; melt workup

*PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

	UNITS		RATE/UNIT		**SENSITIVITY LIKELY	PCT CHANGE	Gov't Acctg
INVESTMENT (MM $)							
BATTERY LIMIT					3.00		3.00
OFFSITE AND ALLOCATED AUX.					1.00		1.00
TOTAL (MM $)					4.00	11	4.00
PROCESSING COST (CENTS/LB)							
DEPRECIATION			10.0	PCT INVST	1.00		-
MM AND RL			5.0	PCT INVST	.50 (1)		.25
OPERATING LABOR	12.00	MEN	8600.0	$/MAN-YR	.26	143	.26
CHEMICAL CONTROL	4.00	MEN	10000.0	$/MAN-YR	.10	370	.10
SUPERVISION	4.00	MEN	12000.0	$/MAN-YR	.12	308	.12
ELECTRICITY	.23	KWH/LB	1.0	CNT/KWH	.23	201	.23
STEAM	4.00	LB /LB	75.0	CNT/M LB	.30	154	.30
WATER	10.00	GAL/LB	10.0	CNT/M GAL	.10	462	.10
FUEL	.01	GAL/LB	7.0	CNT/ GAL	.10	440	.10
TOTAL (CENTS/LB)					2.71		1.46
RAW MATERIAL COST (CENTS/LB)							
UREA	1.23200	LB/LB	4.00	CNT/LB	4.93	9	4.93
AMMONIUM NITRATE	.65600	LB/LB	2.50	CNT/LB	1.64	28	1.64
CATALYST	.00100	LB/LB	150.00	CNT/LB	.15	302	.15
TOTAL (CENTS/LB)					6.72		6.72
PLANT OVERHEAD (CENTS/LB)					.23		.23
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS					9.66		8.41
BY-PRODUCT CREDIT (CENTS/LB)							
AMMONIUM CARBAMATE	.60000	LB/LB	.00	CNT/LB	.00		.00
TOTAL (CENTS/LB)					.00		.00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS					9.66		8.41
						Fringe	1.74
						Price 0% return	10.15¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT

** PERCENT CHANGE NEEDED TO AFFECT RETURN BY [illegible] PERCENTAGE POINTS

(1) 50% is maintenance material

RETURN CALCULATIONS

PLANT INVEST	$	4.0	MM
CORP ALLOC	$	.1	MM
WORKING CAP	$	.6	MM
TOT OP ASSETS	$	4.7	MM

PRICE FOR 0 PCT RETURN 11.4 CENTS/LB
PRICE FOR 20 PCT RETURN 14.1 CENTS/LB
PRICE FOR 30 PCT RETURN 15.5 CENTS/LB

COST STUDY - GUANIDINE NITRATE
CASE 40.610

Basis: Cont. Process; 1 hr. reaction
AN/U = 0.75; aqueous workup
U Yld. = 71%; U Conv. = 66.5%

PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

	UNITS	RATE/[illegible]	LIKELY	SENSITIVITY PCT CHANGE	Gov't Acctg
INVESTMENT (MM $)					
BATTERY LIMIT			3.57		3.57
OFFSITE AND ALLOCATED AUX.			.90		.90
TOTAL (MM $)			4.47	11	4.47
PROCESSING COST (CENTS/LB)					
DEPRECIATION		10.0 PCT INV.*	1.13		-
MM AND RL		5.0 PCT INV.	.56 (1)		.28
OPERATING LABOR	10.00 MEN	8600.0 $/MAN-YR	.21	[illegible]	.21
CHEMICAL CONTROL	4.00 MEN	10000.0 $/MAN-YR	.10	[illegible]	.10
SUPERVISION	4.00 MEN	12000.0 $/MAN-YR	.12	[illegible]	.12
ELECTRICITY	.10 KWH/LB	1.0 CNT/KWH	.10	[illegible]	.10
STEAM	5.00 LB /LB	75.0 CNT/M LB	.37	[illegible]	.37
WATER	8.00 GAL/LB	10.0 CNT/M GAL	[illegible]	[illegible]	.08
FUEL	.01 GAL/LB	7.0 CNT/GAL	.10	[illegible]	.10
TOTAL (CENTS/LB)			2.77		1.36
RAW MATERIAL COST (CENTS/LB)					
UREA	1.38690 LB/LB	4.00 CNT/LB	[illegible]	9	5.54
AMMONIUM NITRATE	.65600 LB/LB	2.50 CNT/LB	1.64	[illegible]	1.64
CATALYST	.00100 LB/LB	150.00 CNT/LB	.15	[illegible]	.15
TOTAL (CENTS/LB)			7.33		7.33
PLANT OVERHEAD (CENTS/LB)			[illegible]		.23
TOTAL MILL COST (CENTS/LB) EX. BY-PRODUCT CREDIT			[illegible]		8.92
BY-PRODUCT CREDIT (CENTS/LB)					
AMMONIUM CARBAMATE	.60000 LB/LB	.00 CNT/LB	.00		.00
TOTAL (CENTS/LB)			.00		.00
TOTAL MILL COST (CENTS/LB) INC. BY-PRODUCT CREDIT			[illegible]		8.92
				Fringe	1.86

Price 0% return 10.78¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT

** PERCENT CHANGE NEEDED TO AFFECT PRICE BY [illegible]

(1) 50% is maintenance material

PRICE [illegible]
PRICE [illegible] 20
PRICE [illegible] 30

COST STUDY - GUANIDINE NITRATE
CASE NO.680

Basis: Cont. Process; 1 hr. reaction
An/U = 0.56; aqueous workup
U Yld. = 62.5%; U Conv. = 68%

*PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

	UNITS	RATE/UNIT	LIKELY	**SENSITIVITY PCT CHANGE	Gov't Acctg
INVESTMENT (MM $)					
BATTERY LIMIT			3.60		3.60
OFFSITE AND ALLOCATED AUX.			.90		.90
TOTAL (MM $)			4.50	11	4.50
PROCESSING COST (CENTS/LB)					
DEPRECIATION		10.0 PCT INVST	1.12		-
MM AND RL		5.0 PCT INVST	.56 (1)		.28
OPERATING LABOR	10.00 MEN	8600.0 $/MAN-YR	.21	194	.21
CHEMICAL CONTROL	4.00 MEN	10000.0 $/MAN-YR	.10	418	.10
SUPERVISION	4.00 MEN	12000.0 $/MAN-YR	.12	348	.12
ELECTRICITY	.10 KWH/LB	1.0 CNT/KWH	.10	500	.10
STEAM	5.00 LB /LB	75.0 CNT/M LB	.37	139	.37
WATER	8.00 GAL/LB	10.0 CNT/M GAL	.08	653	.08
FUEL	.01 GAL/LB	7.0 CNT/ GAL	.10	498	.10
TOTAL (CENTS/LB)			2.78		1.36
RAW MATERIAL COST (CENTS/LB)					
UREA	1.57600 LB/LB	4.00 CNT/LB	6.30	8	6.30
AMMONIUM NITRATE	.65600 LB/LB	2.50 CNT/LB	1.64	31	1.64
CATALYST	.00100 LB/LB	150.00 CNT/LB	.15	341	.15
TOTAL (CENTS/LB)			8.09		8.09
PLANT OVERHEAD (CENTS/LB)			.24		.24
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDIT			11.11		9.69
BY-PRODUCT CREDIT (CENTS/LB)					
AMMONIUM CARBAMATE	.60000 LB/LB	.00 CNT/LB	.00		.00
TOTAL (CENTS/LB)			.00		.00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT			11.11		9.69
				Fringe	1.99

Price 0% return 11.68¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT
** PERCENT CHANGE NEEDED TO AFFECT RETURN BY [illegible] PERCENTAGE POINTS

(1) 50% is maintenance material

RETURN CALCULATION

PLANT INVEST $ 4.[illegible] MM
CORP ALLOC $ .1[illegible] MM
WORKING CAP $ .7[illegible] MM
TOT OP ASSETS $ 5.[illegible] MM

PRICE FOR 0 PCT RETURN 1[illegible] CNT/LB
PRICE FOR 20 PCT RETURN 1[illegible] CNT/LB
PRICE FOR 30 PCT RETURN 1[illegible] CNT/LB

COST STUDY - GUANIDINE NITRATE
CASE NO.630

Basis: Cont. Process; 1 hr. reaction
AN/U = 0.5; aqueous workup
U Yld. = 59%; J Conv. = 68.5%

*PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

				**SENSITIVITY	
	UNITS	RATE/UNIT	LIKELY	PCT CHANGE	Gov't Acctg
INVESTMENT (MM $)					
BATTERY LIMIT			3.57		3.57
OFFSITE AND ALLOCATED AUX.			.90		.90
TOTAL (MM $)			4.47	11	4.47
PROCESSING COST (CENTS/LB)					
DEPRECIATION		10.0 PCT INVST	1.1[illegible] (1)		-
MM AND RL		5.0 PCT INVST	.56		.28
OPERATING LABOR	10.00 MEN	8600.0 $/MAN-YR	.21	1[illegible]	.21
CHEMICAL CONTROL	4.00 MEN	10000.0 $/MAN-YR	.10	417	.10
SUPERVISION	4.00 MEN	12000.0 $/MAN-YR	.12	[illegible]	.12
ELECTRICITY	.10 KWH/LB	1.0 CNT/KWH	.10	[illegible]	.10
STEAM	5.00 LB /LB	75.0 CNT/M LB	.37	130	.37
WATER	8.00 GAL/LB	10.0 CNT/M GAL	.08	65[illegible]	.08
FUEL	.01 [illegible]	7[illegible] CNT/ [illegible]	.10	[illegible]97	.10
TOTAL (CENTS/LB)			[illegible].7[illegible]		1.36
RAW MATERIAL COST (CENTS/LB)					
UREA	1.66800 LB/LB	4.00 CNT/LB	6.67	[illegible]	6.67
AMMONIUM NITRATE	.65600 LB/LB	2.50 CNT/LB	1.64	[illegible]	1.64
CATALYST	.00100 LB/LB	150.00 CNT/LB	.15	[illegible]91	.15
TOTAL (CENTS/LB)			[illegible]		8.46
PLANT OVERHEAD (CENTS/LB)			[illegible]		.23
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDIT			11.[illegible]7		10.05
BY-PRODUCT CREDIT (CENTS/LB)					
AMMONIUM CARBAMATE	.60000 LB/LB	[illegible] CNT/LB	[illegible]		.00
TOTAL (CENTS/LB)			.00		.00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT			11.[illegible]7		10.05
				Fringe	2.03
				Price 0% return	12.08¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT
** PERCENT CHANGE NEEDED TO AFFECT RETURN BY [illegible]

(1) 50% is maintenance material

RETURN CALCULATION

PLANT INVEST [illegible]
CORP ALLOC [illegible]
WORKING CAP [illegible]
[illegible]

PRICE FOR 0 PCT RETURN [illegible]
PRICE FOR 20 PCT RETURN [illegible]
PRICE FOR 30 PCT RETURN [illegible]

COST STUDY - GUANIDINE NITRATE
CASE NO.640

Basis: Cont. Process; 1 hr. reaction
AN/U = 2; aqueous workup
U Yld. = 99%; U Conv. = 55.5%

*PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

	UNITS	RATE/UNIT	LIKELY	**SENSITIVITY PCT CHANGE	Govt Accty
INVESTMENT (MM $)					
BATTERY LIMIT			5.16		5.16
OFFSITE AND ALLOCATED AUX.			1.00		1.00
TOTAL (MM $)			6.16	10	6.16
PROCESSING COST (CENTS/LB)					
DEPRECIATION		10.0 PCT I[illegible]	1.54 (1)		-
RM AND RL		5.0 PCT I[illegible]	.77		.39
OPERATING LABOR	10.00 MEN	8600.0 $/MAN-YR	.21	253	.21
CHEMICAL CONTROL	4.00 MEN	10000.0 $/MAN-YR	.10	544	.10
SUPERVISION	4.00 MEN	12000.0 $/MAN-YR	.12	454	.12
ELECTRICITY	.20 KWH/LB	1.0 CNT/KWH	.20	340	.20
STEAM	6.00 LB /LB	75.0 CNT/M LB	.45	151	.45
WATER	10.00 GAL/LB	10.0 CNT/M GAL	.10	681	.10
FUEL	.02 GAL/LB	7.0 CNT/ GAL	.14	486	.14
TOTAL (CENTS/LB)			3.63		1.71
RAW MATERIAL COST (CENTS/LB)					
UREA	.99500 LB/LB	4.00 CNT/LB	3.98	17	3.98
AMMONIUM NITRATE	.65600 LB/LB	2.50 CNT/LB	1.64	41	1.64
CATALYST	.00200 LB/LB	150.00 CNT/LB	.30	[illegible]	.30
TOTAL (CENTS/LB)			5.92		5.92
PLANT OVERHEAD (CENTS/LB)			.28		.28
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDIT			9.84		7.91
BY-PRODUCT CREDIT (CENTS/LB)					
AMMONIUM CARBAMATE	.61000 LB/LB	.00 CNT/LB	.00		.00
TOTAL (CENTS/LB)			.00		.00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT			9.84		7.91
				Fringe	1.76
				Price 0% return	9.67¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT
** PERCENT CHANGE NEEDED TO AFFECT RETURN BY [illegible] PERCENTAGE POINTS

(1) 50% is maintenance material

RETURN CALCULATIONS

PLANT INVEST $ [illegible]
CORP ALLOC $ [illegible]
WORKING CAP $ [illegible]
TOT OP [illegible] $ [illegible]

PRICE FOR 0 PCT RETURN 11.[illegible] CENTS/LB
PRICE FOR 20 PCT RETURN 15.7 CENTS/LB
PRICE FOR 30 PCT RETURN 17.7 CENTS/LB

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COST STUDY - GUANIDINE NITRATE      Basis:  Cont. Process; 1 hr. reaction
CASE NO.650                                 AN/U = 1.5; aqueous workup
                                            U Yld. = 92.5%; U Conv. = 60%

                            *PRODUCTION COSTS

PLANT CAPACITY     40.0 MM LB/YR                          ***SENSITIVITY
                                                                      Govt
                        UNITS          RATE/ [illegible]  [illegible] Acctg
INVESTMENT (MM $)
 BATTERY LIMIT                                     [illegible]         4.26
 OFFSITE AND ALLOCATED AUX.                        .95                  .95
    TOTAL (MM $)                                   5.[illegible]  11   5.21

PROCESSING COST (CENTS/LB)
 DEPRECIATION                   10.0 PCT INVEST    1.[illegible]         --
 MR AND RL                       5.0 PCT INVEST    [illegible](1)       .33
 OPERATING LABOR    10.00 MEN   8600.0 $/MAN-YR    .21   217            .21
 CHEMICAL CONTROL    4.00 MEN  10000.0 $/MAN-YR    .10   [illegible]    .10
 SUPERVISION         4.00 MEN  12000.0 $/MAN-YR    .12   [illegible]    .12
 ELECTRICITY          .15 KWH/LB   1.0 CNT/KWH     .15   [illegible]    .15
 STEAM               5.00 LB /LB  75.0 CNT/M LB    .37   155            .37
 WATER               9.00 GAL/LB  10.0 CNT/M GAL   .09   [illegible]    .09
 FUEL                 .02 GAL/LB   7.0 CNT/GAL     .12   [illegible]    .12
    TOTAL (CENTS/LB)                               [illegible]         1.49

RAW MATERIAL COST (CENTS/LB)
 UREA             1.06400 LB/LB    4.00 C /LB      [illegible]  12     4.26
 AMMONIUM NITRATE  .65600 LB/LB    2.50 C /LB      1.64  [illegible]   1.64
 CATALYST          .00120 LB/LB  150.00 C /LB      .18   [illegible]    .18
    TOTAL (CENTS/LB)                               [illegible]         6.08

PLANT OVERHEAD (CENTS/LB)                          [illegible]          .26
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS   [illegible].45      7.83

BY-PRODUCT CREDIT (CENTS/LB)
 AMMONIUM CARBAMATE  .60000 LB/LB      .00 C /LB   .00                  .00
    TOTAL (CENTS/LB)                               .00                  .00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS  [illegible]         7.83
                                                         Fringe        1.65
                                                   Price 0% return     9.48 ¢/lb
*   10 YEAR PLANT LIFE, EXISTING SITE
    15 PCT INDIRECT
**  PERCENT CHANGE NEEDED TO AFFECT [illegible]
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(1) 50% is maintenance material

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                              RETURN CALCULATIONS

                           [illegible]
                           [illegible]
                           [illegible]
                           [illegible]

                   PRICE FOR [illegible]               11.[illegible] CENTS/LB
                   PRICE FOR 20 PCT [illegible]        [illegible] CENTS/LB
                   PRICE FOR 30 PCT [illegible]        [illegible] CENTS/LB
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COST STUDY - GUANIDINE NITRATE
CASE NO.810

Basis:
Basic Case
Cont. Process
AN/U/Cat. = 2/2/1.7
U Yld. = 80% U Conv. = 64.5%
AN Yld. = 100% AN Conv. = 32%
By-Prod. Credit = 1¢/lb.

*PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

	UNITS		$/UNIT		LIKELY	**SENSITIVITY PCT CHANGE	Gov't Acctg
INVESTMENT (MM $)							
BATTERY LIMIT					4.22		4.22
OFFSITE AND ALLOCATED AUX.					1.00		1.00
TOTAL (MM $)					5.22	11	5.22
PROCESSING COST (CENTS/LB)							
DEPRECIATION			10.0	PCT INVEST	1.30		-
MM AND RL			5.0	PCT INVEST	.65 (1)		.33
OPERATING LABOR	12.00	MEN	8600.0	$/MAN-YR	.26	182	.26
CHEMICAL CONTROL	4.00	MEN	10000.0	$/MAN-YR	.10	469	.10
SUPERVISION	4.00	MEN	12000.0	$/MAN-YR	.12	391	.12
ELECTRICITY	.20	KWH/LB	1.0	CNT/KWH	.20	[illegible]	.20
STEAM	4.00	LB /LB	75.0	CNT/M LB	.30	195	.30
WATER	10.00	GAL/LB	10.0	CNT/M GAL	.10	586	.10
FUEL	.01	GAL/LB	7.0	CNT/GAL	.10	558	.10
TOTAL (CENTS/LB)					3.14		1.51
RAW MATERIAL COST (CENTS/LB)							
UREA	1.23200	LB/LB	4.00	CNT/LB	4.93	12	4.93
AMMONIUM NITRATE	.65600	LB/LB	2.50	CNT/LB	1.64	35	1.64
CATALYST	.00100	LB/LB	150.00	CNT/LB	.15	383	.15
TOTAL (CENTS/LB)					6.72		6.72
PLANT OVERHEAD (CENTS/LB)					.27		.27
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDIT					10.12		8.50
BY-PRODUCT CREDIT (CENTS/LB)							
AMMONIUM CARBAMATE	.60000	LB/LB	1.00	CNT/LB	.60		.60
TOTAL (CENTS/LB)					.60		.60
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT					9.52		7.90
						Fringe	1.68
						Price 0% return	9.58¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT
** PERCENT CHANGE NEEDED TO AFFECT RETURN [illegible] PERCENTAGE POINTS

(1) 50% is maintenance material

RETURN CALCULATIONS

PLANT INVEST $ 5.2 MM
CORP ALLOC $.[illegible] MM
WORKING CAP $ .6 MM
TOT OF ASSETS $ 6.0 MM

PRICE FOR 0 PCT RETURN 11.[illegible] CENTS/LB
PRICE FOR 20 PCT RETURN 14.7 CENTS/LB
PRICE FOR 30 PCT RETURN 1[illegible] CENTS/LB

COST STUDY - GUANIDINE NITRATE
CASE NO.820

Basis: Cont. Process
AN/U/Cat. = 2/2/1.7
U Yld. = 80% U Conv. = 64.5%
AN Yld. = 100% AN Conv. = 32%
By-Prod. Credit = 2¢/lb.

*PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

	UNITS		RATE/UNIT		[illegible]	**SENSITIVITY PCT CHANGE	Gov't Acctg
INVESTMENT (MM $)							
BATTERY LIMIT					[illegible]		4.22
OFFSITE AND ALLOCATED AUX.					1.00		1.00
TOTAL (MM $)					[illegible]	[illegible]	5.22
PROCESSING COST (CENTS/LB)							
DEPRECIATION			10.0	PCT I[illegible]	1.30		-
MM AND PL			5.0	PCT I[illegible]	.65(1)		.33
OPERATING LABOR	12.00	MEN	8600.0	$/MAN-YR	.26	1[illegible]1	.26
CHEMICAL CONTROL	4.00	MEN	10000.0	$/MAN-YR	.10	467	.10
SUPERVISION	4.00	MEN	12000.0	$/MAN-YR	.12	389	.12
ELECTRICITY	.20	KWH/LB	1.0	CNT/KWH	.20	[illegible]	.20
STEAM	4.00	LB /LB	75.0	CNT/M LB	.30	1[illegible]6	.30
WATER	10.00	GAL/LB	10.0	CNT/M GAL	.10	[illegible]	.10
FUEL	.01	GAL/LB	7.9	CNT / GAL	.10	556	.10
TOTAL (CENTS/LB)					[illegible]		1.51
RAW MATERIAL COST (CENTS/LB)							
UREA	1.23200	LB/LB	4.00	CNT/LB	[illegible].93	12	4.93
AMMONIUM NITRATE	.65600	LB/LB	2.50	CNT/LB	1.64	88	1.64
CATALYST	.00100	LB/LB	150.00	CNT/LB	.15	381	.15
TOTAL (CENTS/LB)					[illegible]		6.72
PLANT OVERHEAD (CENTS/LB)					.27		.27
TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDIT					[illegible]		8.50
BY-PRODUCT CREDIT (CENTS/LB)							
AMMONIUM CARBAMATE	.60000	LB/LB	2.00	CNT/LB	[illegible]		1.20
TOTAL (CENTS/LB)					[illegible]		1.20
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS					[illegible]		7.30
						Fringe	1.58
						Price 0% return	8.88¢/lb

* 10 YEAR PLANT LIFE, EXISTING SITE
15 PCT INDIRECT

** PERCENT CHANGE NEEDED TO AFFECT RETURN BY [illegible]

(1) 50% is maintenance material

[illegible]

PLANT [illegible]
[illegible]
[illegible]
TOT [illegible]

PRICE [illegible] PCT [illegible]
PRICE [illegible] 20 [illegible]
PRICE [illegible] 30 PCT [illegible]

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COST STUDY - GUANIDINE NITRATE   Basis:  Cont. Process
CASE NO.830                              AN/U/Cat. = 2/2/1.7
                                         U Yld. = 80%      U Conv. = 64.5%
                                         AN Yld. = 100%    AN Conv. = 32%
                                         By-Prod. Credit = 3¢/lb.
                             *PRODUCTION COSTS

PLANT CAPACITY     40.0 MM LB/YR                          **SENSITIVITY
                                                                PCT      Govt
                         UNITS            RATE/UNIT   LIKELY  CHANGE    Acctg
INVESTMENT (MM $)
 BATTERY LIMIT                                         4.22              4.22
 OFFSITE AND ALLOCATED AUX.                            1.00              1.00
    TOTAL (MM $)                                       5.22     11       5.22

PROCESSING COST (CENTS/LB)
 DEPRECIATION                       10.0 PCT INVST     1.30               -
 MM AND RL                           5.0 PCT INVST      .65(1)           .33
 OPERATING LABOR      12.00 MEN   8600.0 $/MAN-YR       .26    181       .26
 CHEMICAL CONTROL      4.00 MEN  10000.0 $/MAN-YR       .10    466       .10
 SUPERVISION           4.00 MEN  12000.0 $/MAN-YR       .12    388       .12
 ELECTRICITY            .20 KWH/LB   1.0 CNT/KWH        .20    291       .20
 STEAM                 4.00 LB /LB  75.0 CNT/M LB       .30    194       .30
 WATER                10.00 GAL/LB  10.0 CNT/M GAL      .10    582       .10
 FUEL                   .01 GAL/LB   7.0 CNT/ GAL       .10    554       .10
    TOTAL (CENTS/LB)                                   3.14              1.51

RAW MATERIAL COST (CENTS/LB)
 UREA               1.23200 LB/LB      4.00 CNT/LB     4.93     12       4.93
 AMMONIUM NITRATE    .65600 LB/LB      2.50 CNT/LB     1.64     35       1.64
 CATALYST            .00100 LB/LB    150.00 CNT/LB      .15    380        .15
    TOTAL (CENTS/LB)                                   6.72              6.72

PLANT OVERHEAD (CENTS/LB)                               .27               .27
TOTAL MILL COST (CENTS/LB) EX  BY-PRODUCT CREDITS     10.12              8.50

BY-PRODUCT CREDIT (CENTS/LB)
 AMMONIUM CARBAMATE  .60000 LB/LB      3.00 CNT/LB     1.80              1.80
    TOTAL (CENTS/LB)                                   1.80              1.80
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS      8.32              6.70
                                                            Fringe       1.48
                                                    Price 0% return    8.18¢/lb
*   10 YEAR PLANT LIFE, EXISTING SITE
    15 PCT INDIRECT
**  PERCENT CHANGE NEEDED TO AFFECT RETURN BY 2 PERCENTAGE POINTS

(1) 50%is maintenance material       RETURN CALCULATIONS

                       PLANT INVEST     $  [illegible]
                       CORP ALLOC       $  [illegible]
                       WORKING CAP      $  [illegible]
                       TOT OP ASSETS    $  5.[illegible]

                PRICE FOR  0 PCT RETURN      [illegible] CENTS/LB
                PRICE FOR 20 PCT RETURN      1[illegible] CENTS/LB
                PRICE FOR 30 PCT RETURN      1[illegible] CENTS/LB
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COST STUDY - GUANIDINE NITRATE                      Basic Case
CASE NO.910                                 Basis:  Cont. Process
                                                    AN/U/Cat. = 2/2/1.7
                                                    U Yld. = 80%    U Conv. = 64.5%
                                                    AN Yld. = 100%  AN Conv. = 32%
                                    PRODUCTION COSTS        Urea = 2¢/lb.

PLANT CAPACITY     40.0 MM LB/YR*                              ***SENSITIVITY
                                                                     PCT      Govt
                            UNITS          RATE/UNIT     YEARLY    CHANGE    Acctg
INVESTMENT (MM $)
 BATTERY LIMIT                                          [illegible]          4.22
 OFFSITE AND ALLOCATED AUX.                                1.10              1.00
    TOTAL (MM $)                                        5.[illegible]  10    5.22

PROCESSING COST (CENTS/LB)
 DEPRECIATION                            10.0 PCT INV      1.30(1)             -
 MM AND PL                                5.0 PCT INV       .65              .33
 OPERATING LABOR         12.00 MEN      8600.0 $/MAN-YR     .26     177      .26
 CHEMICAL CONTROL         4.00 MEN     10000.0 $/MAN-YR     .10 [illegible]  .10
 SUPERVISION              4.00 MEN     12000.0 $/MAN-YR     .12 [illegible]  .12
 ELECTRICITY               .20 KWH/LB     1.0 CENTS/KWH     .20 [illegible]  .20
 STEAM                    4.00 LB /LB    75.0 CENTS/MLB     .30 [illegible]  .30
 WATER                   10.00 GAL/LB    10.0 CENTS/MGAL    .10 [illegible]  .10
 FUEL                      .01 GAL/LB     7.0 [illegible]   .[illegible]     .10
    TOTAL (CENTS/LB)                                    [illegible]         1.51

RAW MATERIAL COST (CENTS/LB)
 UREA                   1.23200 LB/LB     2.[illegible] CENTS/LB [illegible] 2.46
 AMMONIUM NITRATE        .65600 LB/LB     2.50 CENTS/LB    1.64              1.64
 CATALYST                .00100 LB/LB   150.00 CENTS/LB     .15 [illegible]  .15
    TOTAL (CENTS/LB)                                       4.25             4.25

PLANT OVERHEAD (CENTS/LB)                                   .27              .27
TOTAL MILL COST (CENTS/LB) EX  BY-PRODUCT CREDITS          7.66             6.03

BY-PRODUCT CREDIT (CENTS/LB)
 AMMONIUM CARBAMATE  .60000 LB/LB        .01 CENTS/LB   [illegible]          .00
    TOTAL (CENTS/LB)                                    [illegible]          .00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS          7.66             6.03
                                                            Fringe          1.34
                                                  Price 0% return    7.37¢/lb
*   10 YEAR PLANT LIFE, EXISTING SITE
    15 PCT INDIRECT
**  PERCENT CHANGE NEEDED TO AFFECT RETURN BY [illegible]

(1) 50% is maintenance material             RETURN CALCULATIONS

                                  PLANT INVEST          [illegible]
                                  [illegible]           [illegible]
                                  WORKING CAP           [illegible]
                                  TOTAL [illegible]     [illegible]

                         PRICE FOR [illegible]          [illegible]
                         PRICE FOR 20 PCT [illegible]   [illegible]
                         PRICE FOR 30 PCT [illegible]   [illegible]
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COST STUDY - GUANIDINE NITRATE                 Basis:  Cont. Process
CASE NO. 920                                           AN/U/Cat. = 2/2/1.7
                                                       U Yld. = 80%   U Conv. = 64.5%
                                                       AN Yld. = 100% AN Conv. = 32%
                                                       Urea = 3¢/lb.
                                   *PRODUCTION COSTS

PLANT CAPACITY     40.0 MM LB/YR                                **SENSITIVITY
                                                                       PCT        Govt
                            UNITS               RATE/UNIT    SIMPLY   CHANGE      Acctg
INVESTMENT (MM $)
 BATTERY LIMIT                                                 4.22                4.22
 OFFSITE AND ALLOCATED AUX.                                    1.00                1.00
    TOTAL (MM $)                                               5.22      11        5.22

PROCESSING COST (CENTS/LB)
 DEPRECIATION                               10.0 PCT INVST     1.30                 -
 MM AND RL                                   5.0 PCT INVST      .65 (1)             .33
 OPERATING LABOR       12.00 MEN          8600.0 $/MAN-YR       .26     180         .26
 CHEMICAL CONTROL       4.00 MEN         10000.0 $/MAN-YR       .10     464         .10
 SUPERVISION            4.00 MEN         12000.0 $/MAN-YR       .12     387         .12
 ELECTRICITY             .20 KWH/LB          1.0 CNT/KWH        .20     290         .20
 STEAM                  4.00 LB /LB         75.0 CNT/M LB       .30     193         .30
 WATER                 10.00 GAL/LB         10.0 CNT/MGAL       .10     580         .10
 FUEL                    .01 GAL/LB          7.0 CNT/ GAL       .10     552         .10
    TOTAL (CENTS/LB)                                           3.14                1.51

RAW MATERIAL COST (CENTS/LB)
 UREA                1.23200 LB/LB          3.00 CNT/LB        3.70      15        3.70
 AMMONIUM NITRATE     .65600 LB/LB          2.50 CNT/LB        1.64      35        1.64
 CATALYST             .00190 LB/LB        150.00 CNT/LB         .15     379         .15
    TOTAL (CENTS/LB)                                           5.49                5.49

PLANT OVERHEAD (CENTS/LB)                                       .27                 .27
TOTAL MILL COST (CENTS/LB) EX  BY-PRODUCT CREDITS              8.89                7.27

BY-PRODUCT CREDIT (CENTS/LB)
 AMMONIUM CARBAMATE  .60000 LB/LB            .00 CNT/LB         .00                 .00
    TOTAL (CENTS/LB)                                            .00                 .00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS              8.89                7.27

                                                               Fringe          1.61
*   10 YEAR PLANT LIFE, EXISTING SITE                 Price 0% return 8.88¢/lb
    15 PCT INDIRECT
**  PERCENT CHANGE NEEDED TO AFFECT RETURN BY [illegible] PERCENTAGE POINTS

(1) 50% is maintenance material          RETURN CALCULATIONS

                                         PLANT INVEST     $   [illegible] MM
                                         CORP ALLOC       $   [illegible]
                                         WORKING CAP      $   [illegible]
                                         TOT OP ASSETS    $   [illegible] MM

                               PRICE FOR  0 PCT RETN       [illegible] CENTS/LB
                               PRICE FOR 20 PCT RETURN     [illegible] CENTS/LB
                               PRICE FOR 30 PCT RETURN     [illegible] CENTS/LB
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COST STUDY - GUANIDINE NITRATE     Basis:  Cont. Process; 1 hr. reaction
CASE NO.710                                AN/U/Cat. = 2/2/1.7
                                           Aqueous workup, 3-stage agit. reactor
                                           U Yld. = 80%; U Conv. = 64.5%

                              *PRODUCTION COSTS

PLANT CAPACITY     40.0 MM LB/YR                               **SENSITIVITY
                                                                     PCT     Gov't
                              UNITS           RATE/UNIT      CIRCLY  CHANGE   Acctg
INVESTMENT (MM $)
 BATTERY LIMIT                                                 2.49            2.49
 OFFSITE AND ALLOCATED AUX.                                     .90             .90
   TOTAL (MM $)                                                3.39     11     3.30

PROCESSING COST (CENTS/LB)
 DEPRECIATION                              10.0 PCT INVST       .85 (1)          -
 MM AND RL                                  5.0 PCT INVST       .42             .21
 OPERATING LABOR        10.00 MEN        8600.0 $/MAN-YR        .21    148      .21
 CHEMICAL CONTROL        4.00 MEN       10000.0 $/MAN-YR        .10    319      .10
 SUPERVISION             4.00 MEN       12000.0 $/MAN-YR        .12    266      .12
 ELECTRICITY              .13 KWH/LB        1.0 CNT/KWH         .13    [illegible] .13
 STEAM                   5.00 LB /LB       75.0 CNT/M LB        .37    106      .37
 WATER                   8.00 GAL/LB       10.0 CNT/M GAL       .08    [illegible] .08
 FUEL                     .01 GAL/LB        7.6 CNT/ GAL        .10    [illegible] .10
   TOTAL (CENTS/LB)                                            [illegible]     1.32

RAW MATERIAL COST (CENTS/LB)
 UREA                 1.23200 LB/LB        4.00 CNT/LB         4.93      8     4.93
 AMMONIUM NITRATE      .65600 LB/LB        2.50 CNT/LB         1.64 [illegible] 1.64
 CATALYST              .00100 LB/LB      150.00 CNT/LB          .15 [illegible]  .15
   TOTAL (CENTS/LB)                                            6.72            6.72

PLANT OVERHEAD (CENTS/LB)                                     [illegible]       .20
TOTAL MILL COST (CENTS/LB) EX  BY-PRODUCT CREDIT              [illegible]      8.24

BY-PRODUCT CREDIT (CENTS/LB)
 AMMONIUM CARBAMATE    .60000 LB/LB         .00 CNT/LB          .00             .00
   TOTAL (CENTS/LB)                                             .00             .00
TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT              [illegible]      8.24
                                                                Fringe         1.68
                                                          Price 0% return     9.92¢/lb
*   10 YEAR PLANT LIFE, EXISTING SITE
    15 PCT INDIRECT
**  PERCENT CHANGE NEEDED TO AFFECT [illegible]

(1) 50% is maintenance material                [illegible] CALCULATIONS

                                      [illegible]          [illegible]
                                      [illegible]          [illegible]
                                      [illegible]          [illegible]
                                      [illegible]          [illegible]

                       PRICE [illegible]  0 PCT [illegible]        11.[illegible]
                       PRICE [illegible] 20 PCT [illegible]        1[illegible]
                       PRICE [illegible] 30 PCT [illegible]        1[illegible]
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APPENDIX I-6. MATHEMATICAL REACTOR PRINTOUTS

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GUANIDINE NITRATE PROJECT
PACKED BED TUBULAR REACTOR

HOUDRY BEADS
  BULK DENSITY =  7.37 GRAMS/CU. IN.
  VOID FRACTION = .437
TUBE DIAMETER =  2.00 INCHES
FEED TEMPERATURE = 190.0 C.
JACKET TEMPERATURE = 195.0 C.
OVERALL HEAT TRANSFER COEFFICIENT =  1.08 CAL./SQ.IN.-MIN.-C.

DISTANCE   MOLAR FLOW RATES          MOLE      FRACTIONS          CONVERSION   YIELD      TEMPERATURE
 INCHES      MOLES/MINUTE          AMMONIUM    UREA   GUANIDINE   M.U REAC/   M. GN/       DEG. C.
            MELT        GAS        NITRATE                NITRATE   M.U FED     M. U REAC

   .000     .415       .000        .4730      .4730     .0540       .0000      .0000          190.0
   .500     .412       .003        .4746      .4686     .0569       .0176      .2865          189.5
  1.000     .409       .006        .4761      .4643     .0597       .0344      .2874          189.1
  1.500     .405       .009        .4775      .4601     .0624       .0515      .2893          188.8
  2.000     .402       .011        .4789      .4560     .0651       .0650      .2906          188.6
  2.500     .399       .014        .4802      .4520     .0678       .0810      .2920          188.4
  5.000     .386       .027        .4865      .4323     .0812       .1516      .2984          188.1
  7.500     .373       .039        .4922      .4129     .0949       .2155      .3049          188.2
 10.000     .361       .051        .4975      .3936     .1091       .2758      .3115          188.3
 12.500     .350       .062        .5019      .3746     .1235       .3326      .3183          188.5
 15.000     .340       .074        .5058      .3559     .1383       .3843      .3252          188.7
 17.500     .330       .085        .5091      .3377     .1532       .4319      .3323          188.9
 20.000     .322       .095        .5117      .3200     .1682       .4756      .3395          189.1
 22.500     .314       .105        .5137      .3030     .1833       .5157      .3468          189.3
 25.000     .307       .115        .5150      .2867     .1983       .5522      .3542          189.5
 27.500     .300       .125        .5157      .2711     .2132       .5855      .3615          189.7
 30.000     .294       .134        .5158      .2564     .2278       .6158      .3689          189.9
 32.500     .289       .143        .5153      .2425     .2422       .6434      .3763          190.1
 35.000     .283       .151        .5143      .2294     .2563       .6681      .3836          190.3
 37.500     .280       .159        .5129      .2171     .2700       .6918      .3905          190.5
 40.000     .276       .167        .5111      .2056     .2833       .7116      .3979          190.7
 42.500     .272       .174        .5089      .1943     .2962       .7335      .4042          190.9
 45.000     .269       .181        .5058      .1840     .3086       .7472      .4118          191.1
 47.500     .266       .188        .5037      .1756     .3207       .7626      .4186          191.2
 48.000     .265       .189        .5031      .1739     .3230       .7655      .4199          191.3

MELT FEED RATE =  4.00 LB./HR.                                TOTAL CATALYST WEIGHT = 1111.37 GRAMS
FEED WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .5197            NOMINAL RESIDENCE TIME =  92.62 MINUTES
                                     UREA =  .3898            RATE CONSTANT FOR GN
                        GUANIDINE NITRATE =  .0905                FREQUENCY FACTOR =   .1511E 13
PRODUCT RATE =  5.157 LB./HR.                                     ACTIVATION ENERGY/R=   .1656E 05
PRODUCT WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .4468         RATE CONSTANT FOR UREA DECOMPOSITION
                                        UREA =  .1158             FREQUENCY FACTOR =   .2000E 14
                           GUANIDINE NITRATE =  .4374             ACTIVATION ENERGY/R=   .1680E 05
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    GUANIDINE NITRATE PROJECT
    PACKED BED TUBULAR REACTOR

HOUDRY BEADS
  BULK DENSITY =  7.37 GRAMS/CU. IN.
  VOID FRACTION = .437
TUBE DIAMETER =  2.00 INCHES
FEED TEMPERATURE = 190.0 C.
JACKET TEMPERATURE = 195.0 C.
OVERALL HEAT TRANSFER COEFFICIENT =  1.08 CAL./SQ.IN.-MIN.-C.

DISTANCE   MOLAR FLOW RATES          MOLE       FRACTIONS           CONVERSION   YIELD     TEMPERATURE
 INCHES     MOLES/MINUTE        AMMONIUM      UREA   GUANIDINE   M.U REAC/    M. GN/      DEG. C.
            MELT       GAS        NITRATE               NITRATE    M.U FED    M. U REAC

   .000     .831      .000       .4730       .4730     .0540       .0000      .0000        190.0
   .500     .827      .003       .4738       .4708     .0554       .0089      .2858        189.7
  1.000     .824      .006       .4746       .4686     .0569       .0176      .2865        189.5
  1.500     .820      .009       .4753       .4664     .0583       .0251      .2872        189.3
  2.000     .817      .012       .4761       .4643     .0597       .0344      .2879        189.1
  2.500     .814      .014       .4768       .4622     .0610       .0425      .2886        188.9
  5.000     .799      .028       .4802       .4520     .0678       .0810      .2920        188.4
  7.500     .785      .041       .4834       .4421     .0745       .1172      .2052        188.2
 10.000     .771      .053       .4865       .4323     .0812       .1516      .2984        188.1
 12.500     .758      .066       .4894       .4226     .0880       .1847      .3016        188.2
 15.000     .746      .078       .4922       .4129     .0949       .2155      .3049        188.2
 17.500     .734      .090       .4948        4032     .1020       .2472      .3082        188.3
 20.000     .722      .102       .4973       .3936     .1091       .2756      .3115        188.3
 22.500     .711      .113       .4997       .3841     .1162       .3052      .3149        188.4
 25.000     .700      .125       .5019       .3746     .1235       .3325      .3183        188.5
 27.500     .690      .136       .5039       .3652     .1309       .3590      .3217        188.6
 30.000     .680      .147       .5058       .3559     .1383       .3843      .3252        188.7
 32.500     .670      .158       .5076       .3467     .1457       .4086      .3288        188.8
 35.000     .661      .169       .5091       .3377     .1532       .4310      .3323        188.9
 37.500     .652      .180       .5105       .3288     .1607       .4543      .3359        189.0
 40.000     .644      .190       .5117       .3200     .1682       .4756      .3395        189.1
 42.500     .636      .201       .5128       .3114     .1758       .4951      .3432        189.2
 45.000     .628      .211       .5137       .3030     .1833       .5157      .3468        189.3
 47.500     .621      .221       .5144       .2947     .1908       .5344      .3505        189.4
 48.000     .619      .223       .5146       .2931     .1923       .5380      .3512        189.4

MELT FEED RATE =  8.00 LB./HR.                                  TOTAL CATALYST WEIGHT = 1111.37 GRAMS
FEED WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .5107              NOMINAL RESIDENCE TIME =  46.31 MINUTES
                                     UREA =  .3808              RATE CONSTANT FOR GN
                        GUANIDINE NITRATE =  .0905                  FREQUENCY FACTOR =   .1511E 13
PRODUCT RATE =  6.735 LB./HR.                                       ACTIVATION ENERGY/R=   .1655E 05
PRODUCT WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .5007           RATE CONSTANT FOR UREA DECOMPOSITION
                                        UREA =  .2139               FREQUENCY FACTOR =   .2009E 14
                           GUANIDINE NITRATE =  .2854               ACTIVATION ENERGY/R=   .1680E 05
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     GUANIDINE NITRATE PROJECT
    PACKED BED TUBULAR REACTOR

 HOUDRY BEADS
   BULK DENSITY =  7.37 GRAMS/CU. IN.
   VOID FRACTION = .437
 TUBE DIAMETER =  2.00 INCHES
 FEED TEMPERATURE = 190.0 C.
 JACKET TEMPERATURE = 195.0 C.
 OVERALL HEAT TRANSFER COEFFICIENT =  1.08 CAL./SQ.IN.-MIN.-C.

 DISTANCE    MOLAR FLOW RATES          MOLE     FRACTIONS           CONVERSION   YIELD      TEMPERATURE
  INCHES       MOLES/MINUTE          AMMONIUM     UREA   GUANIDINE  M.U REAC/   M. GN/        DEG. C.
               MELT        GAS        NITRATE              NITRATE  M.U FED    M. U REAC

    .000       .432       .000        .5000     .5000    .0000     .0000      .0000          190.0
    .500       .428       .003        .5022     .4952    .0026     .0180      .2711          189.3
   1.000       .424       .006        .5042     .4907    .0051     .0356      .2725          188.8
   1.500       .420       .010        .5062     .4862    .0075     .0535      .2738          188.5
   2.000       .417       .012        .5081     .4819    .0100     .0698      .2751          188.2
   2.500       .414       .015        .5100     .4776    .0124     .0856      .2763          188.0
   5.000       .398       .029        .5188     .4568    .0244     .1590      .2824          187.6
   7.500       .383       .042        .5270     .4361    .0369     .2265      .2886          187.6
  10.000       .370       .055        .5347     .4155    .0498     .2892      .2949          187.8
  12.500       .357       .068        .5417     .3949    .0634     .3474      .3015          187.9
  15.000       .345       .080        .5481     .3745    .0773     .4012      .3082          188.1
  17.500       .335       .092        .5538     .3545    .0917     .4509      .3151          188.3
  20.000       .325       .104        .5587     .3359    .1054     .4954      .3222          188.5
  22.500       .316       .115        .5628     .3160    .1212     .5380      .3294          188.7
  25.000       .308       .126        .5661     .2978    .1361     .5759      .3366          189.0
  27.500       .300       .136        .5685     .2804    .1511     .6103      .3440          189.2
  30.000       .293       .146        .5702     .2640    .1658     .6414      .3514          189.4
  32.500       .287       .156        .5711     .2484    .1805     .6625      .3587          189.6
  35.000       .282       .165        .5713     .2338    .1949     .6949      .3661          189.9
  37.500       .277       .174        .5709     .2201    .2090     .7178      .3734          190.1
  40.000       .273       .182        .5699     .2073    .2228     .7384      .3806          190.3
  42.500       .268       .190        .5684     .1955    .2361     .7570      .3876          190.5
  45.000       .265       .198        .5665     .1845    .2490     .7738      .3946          190.7
  47.500       .262       .205        .5642     .1743    .2615     .7839      .4014          190.9
  48.000       .261       .207        .5637     .1724    .2639     .7917      .4028          190.9

 MELT FEED RATE =  4.00 LB./HR.                                     TOTAL CATALYST WEIGHT = 1111.37 GRAMS
 FEED WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .5714                 NOMINAL RESIDENCE TIME =  49.05 MINUTES
                                     UREA =  .4286                  RATE CONSTANT FOR GN
                        GUANIDINE NITRATE =  .0000                     FREQUENCY FACTOR =   .1311E 13
 PRODUCT RATE =  3.025 LB./HR.                                         ACTIVATION ENERGY/R=   .1655E 05
 PRODUCT WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .5146              RATE CONSTANT FOR UREA DECOMPOSITION
                                         UREA =  .1180                 FREQUENCY FACTOR =   .2009E 14
                            GUANIDINE NITRATE =  .3674                 ACTIVATION ENERGY/R=   .1669E 05
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    GUANIDINE NITRATE PROJECT
   PACKED BED TUBULAR REACTOR

HOUDRY BEADS
  BULK DENSITY =  7.37 GRAMS/CU. IN.
  VOID FRACTION = .437
TUBE DIAMETER =  2.00 INCHES
FEED TEMPERATURE = 190.0 C.
JACKET TEMPERATURE = 195.0 C.
OVERALL HEAT TRANSFER COEFFICIENT =  1.08 CAL./SQ.IN.-MIN.-C.


DISTANCE   MOLAR FLOW RATES          MOLE      FRACTIONS              CONVERSION   YIELD     TEMPERATURE
 INCHES      MOLES/MINUTE         AMMONIUM     UREA   GUANIDINE   M.U REAC/    M. GN/      DEG. C.
            MELT         GAS       NITRATE                NITRATE     M.U FED    M. U REAC

    .000    .648        .000        .5000      .5000     .0000      .0000      .0000          190.0
    .500    .644        .003        .5015      .4968     .0017      .0127      .2706          189.5
   1.000    .640        .007        .5029      .4937     .0034      .0249      .2716          189.2
   1.500    .636        .010        .5042      .4907     .0051      .0356      .2725          188.8
   2.000    .632        .013        .5056      .4877     .0067      .0480      .2734          188.6
   2.500    .629        .016        .5069      .4848     .0083      .0590      .2742          188.4
   5.000    .612        .030        .5130      .4706     .0163      .1109      .2784          187.8
   7.500    .596        .044        .5188      .4568     .0244      .1590      .2824          187.6
  10.000    .582        .057        .5243      .4430     .0326      .2046      .2865          187.6
  12.500    .568        .070        .5296      .4293     .0411      .2479      .2907          187.7
  15.000    .554        .083        .5347      .4155     .0498      .2892      .2949          187.8
  17.500    .542        .096        .5394      .4017     .0588      .3285      .2993          187.9
  20.000    .529        .108        .5439      .3881     .0680      .3658      .3037          188.0
  22.500    .518        .120        .5481      .3745     .0773      .4012      .3082          188.1
  25.000    .507        .132        .5520      .3611     .0869      .4346      .3128          188.2
  27.500    .497        .144        .5555      .3479     .0966      .4665      .3174          188.4
  30.000    .487        .155        .5587      .3349     .1064      .4964      .3222          188.5
  32.500    .478        .167        .5615      .3222     .1162      .5246      .3269          188.7
  35.000    .469        .178        .5640      .3099     .1262      .5510      .3318          188.8
  37.500    .461        .188        .5661      .2978     .1361      .5759      .3366          189.0
  40.000    .454        .199        .5678      .2861     .1461      .5992      .3415          189.1
  42.500    .447        .209        .5691      .2748     .1561      .6210      .3465          189.3
  45.000    .440        .219        .5702      .2640     .1659      .6414      .3514          189.4
  47.500    .434        .229        .5709      .2535     .1757      .6605      .3563          189.5
  48.000    .433        .231        .5710      .2514     .1776      .6641      .3573          189.6

MELT FEED RATE =  6.00 LB./HR.                                   TOTAL CATALYST WEIGHT = 1111.37 GRAMS
FEED WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .5714               NOMINAL RESIDENCE TIME =  59.37 MINUTES
                                     UREA =  .4286               RATE CONSTANT FOR GN
                        GUANIDINE NITRATE =  .0000                  FREQUENCY FACTOR =   .1311E 13
PRODUCT RATE =  4.719 LB./HR.                                       ACTIVATION ENERGY/R=   .1655E 05
PRODUCT WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .5541            RATE CONSTANT FOR UREA DECOMPOSITION
                                        UREA =  .1830               FREQUENCY FACTOR =   .2009E 14
                           GUANIDINE NITRATE =  .2629               ACTIVATION ENERGY/R=   .1689E 05
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  GUANIDINE NITRATE PROJECT
 PACKED BED TUBULAR REACTOR

HOUDRY BEADS
  BULK DENSITY =  7.37 GRAMS/CU. IN.
  VOID FRACTION = .437
TUBE DIAMETER =  2.00 INCHES
FEED TEMPERATURE = 190.0 C.
JACKET TEMPERATURE = 195.0 C.
OVERALL HEAT TRANSFER COEFFICIENT =  1.08 CAL./SQ.IN.-MIN.-C.


DISTANCE   MOLAR FLOW RATES          MOLE      FRACTIONS             CONVERSION   YIELD     TEMPERATURE
 INCHES      MOLES/MINUTE          AMMONIUM     UREA  GUANIDINE  M.U REAC/   M. GN/       DEG. C.
             MELT       GAS         NITRATE              NITRATE    M.U FED  M. U REAC

   .000      .864      .000         .5000      .5000     .0000      .0000     .0000        190.0
   .500      .860      .003         .5011      .4976     .0013      .0096     .2704        189.6
  1.000      .856      .007         .5022      .4952     .0026      .0189     .2711        189.5
  1.500      .852      .010         .5032      .4929     .0038      .0279     .2718        189.1
  2.000      .848      .013         .5042      .4907     .0051      .0366     .2725        188.8
  2.500      .844      .016         .5052      .4884     .0063      .0452     .2731        188.6
  5.000      .827      .031         .5100      .4776     .0124      .0856     .2763        188.0
  7.500      .811      .045         .5145      .4672     .0183      .1232     .2794        187.7
 10.000      .795      .058         .5188      .4568     .0244      .1590     .2824        187.6
 12.500      .780      .072         .5230      .4465     .0306      .1934     .2855        187.6
 15.000      .766      .085         .5270      .4361     .0369      .2255     .2886        187.6
 17.500      .752      .098         .5309      .4258     .0433      .2584     .2917        187.7
 20.000      .739      .111         .5347      .4155     .0498      .2892     .2949        187.8
 22.500      .726      .123         .5383      .4052     .0565      .3188     .2982        187.9
 25.000      .714      .136         .5417      .3949     .0634      .3474     .3015        187.9
 27.500      .702      .148         .5450      .3847     .0703      .3748     .3048        188.0
 30.000      .691      .160         .5481      .3745     .0773      .4012     .3082        188.1
 32.500      .680      .172         .5511      .3644     .0845      .4256     .3116        188.2
 35.000      .669      .184         .5538      .3545     .0917      .4500     .3151        188.3
 37.500      .659      .196         .5564      .3446     .0990      .4741     .3186        188.4
 40.000      .650      .207         .5587      .3340     .1054      .4954     .3222        188.5
 42.500      .640      .219         .5609      .3254     .1138      .5177     .3257        188.6
 45.000      .632      .230         .5628      .3160     .1212      .5380     .3294        188.7
 47.500      .623      .241         .5645      .3068     .1257      .5574     .3330        188.8
 48.000      .622      .243         .5648      .3050     .1302      .5612     .3337        188.9

MELT FEED RATE =  8.00 LB./HR.                                   TOTAL CATALYST WEIGHT = 1111.37 GRAMS
FEED WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .5714               NOMINAL RESIDENCE TIME =  44.52 MINUTES
                                     UREA =  .4286               RATE CONSTANT FOR GN
                        GUANIDINE NITRATE =  .0000                  FREQUENCY FACTOR =   .1311E 13
PRODUCT RATE =  6.525 LB./HR.                                       ACTIVATION ENERGY/R=   .1655E 05
PRODUCT WEIGHT FRACTIONS =  AMMONIUM NITRATE =  .5694            RATE CONSTANT FOR UREA DECOMPOSITION
                                        UREA =  .2306               FREQUENCY FACTOR =   .2009E 14
                           GUANIDINE NITRATE =  .2001               ACTIVATION ENERGY/R=   .1689E 05
```

APPENDIX II

PHASE III, PART 1

GUANIDINE NITRATE PILOT PLANT OPERATIONS

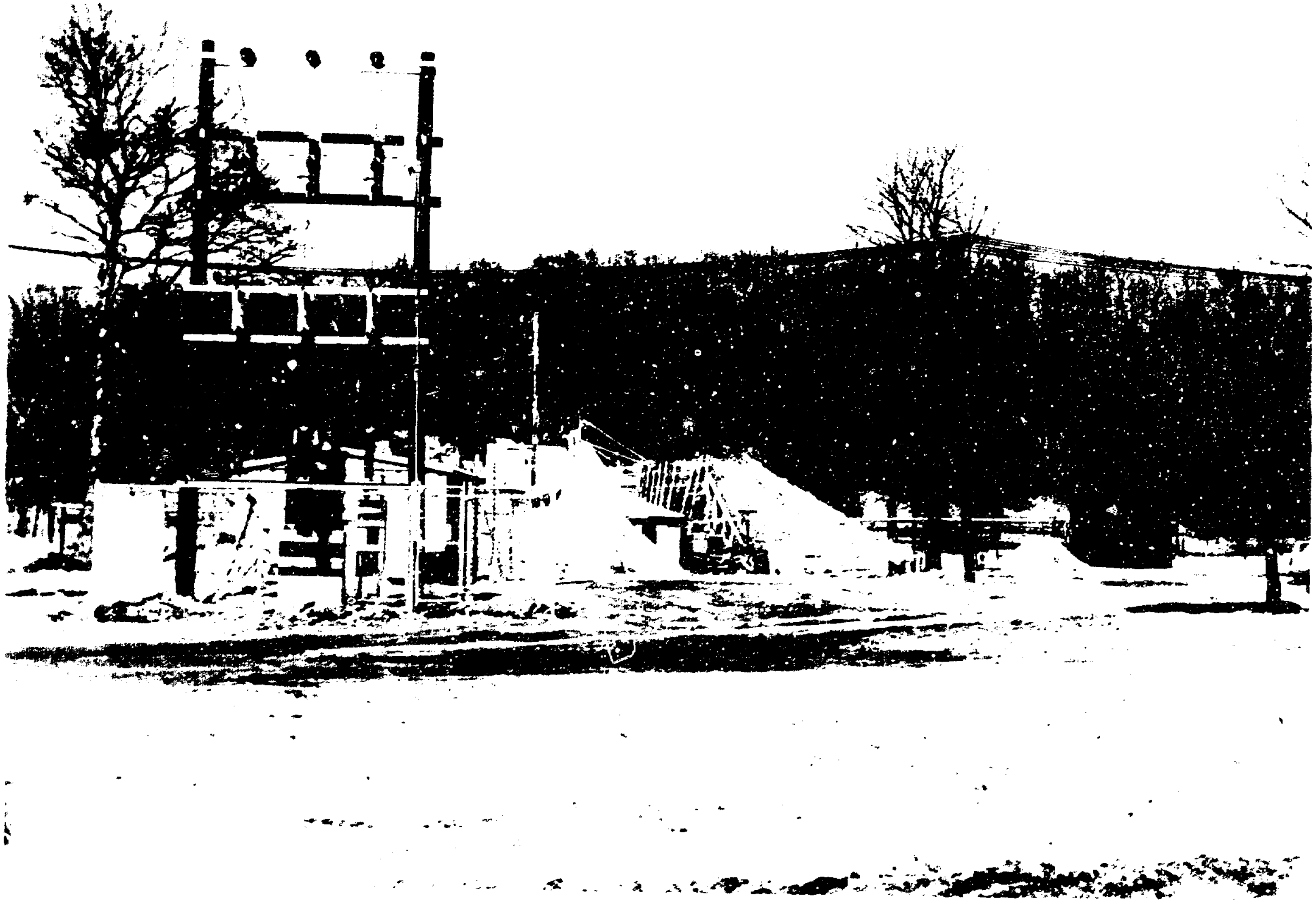

Figure II-1. Guanidine Nitrate Pilot Plant

Figure II-2. High Pressure Steam Boilers

Figure II-[illegible] Urea/Ammonium Nitrate Melt and Feed Systems

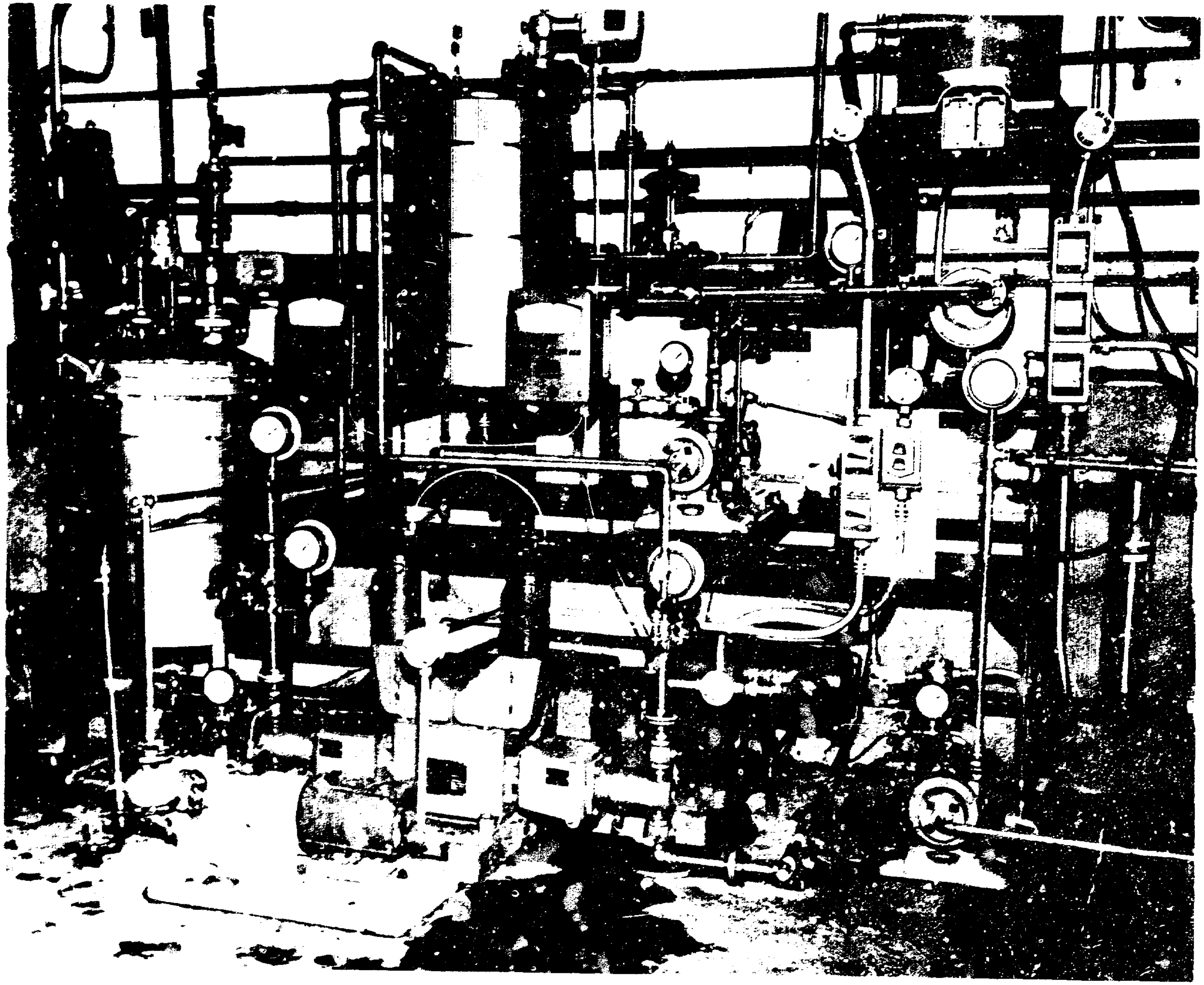

Figure 11-a Urea Ammonium Nitrate Feed System

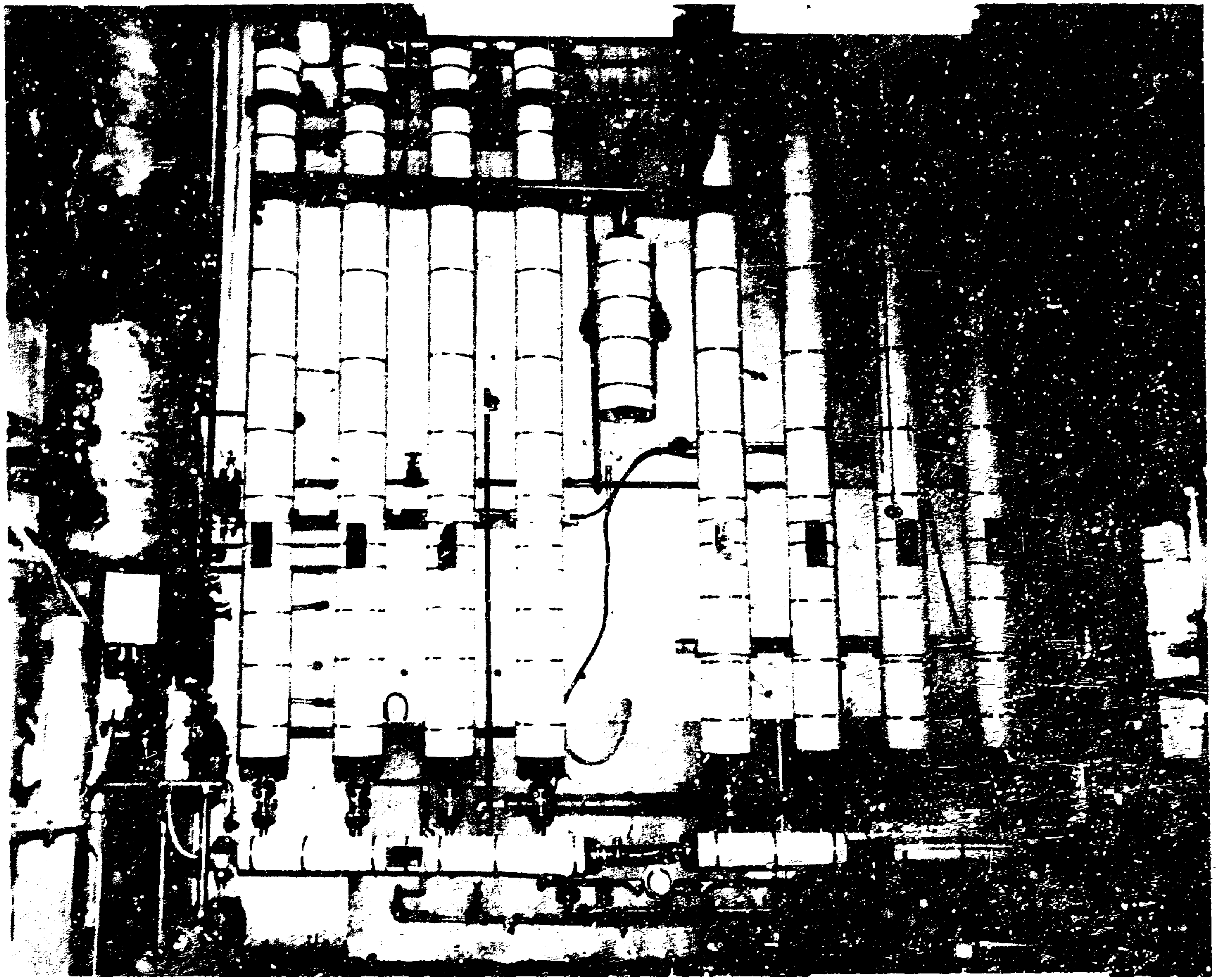

Figure II-5. Guanidine Nitrate Catalytic Tubular Reactors

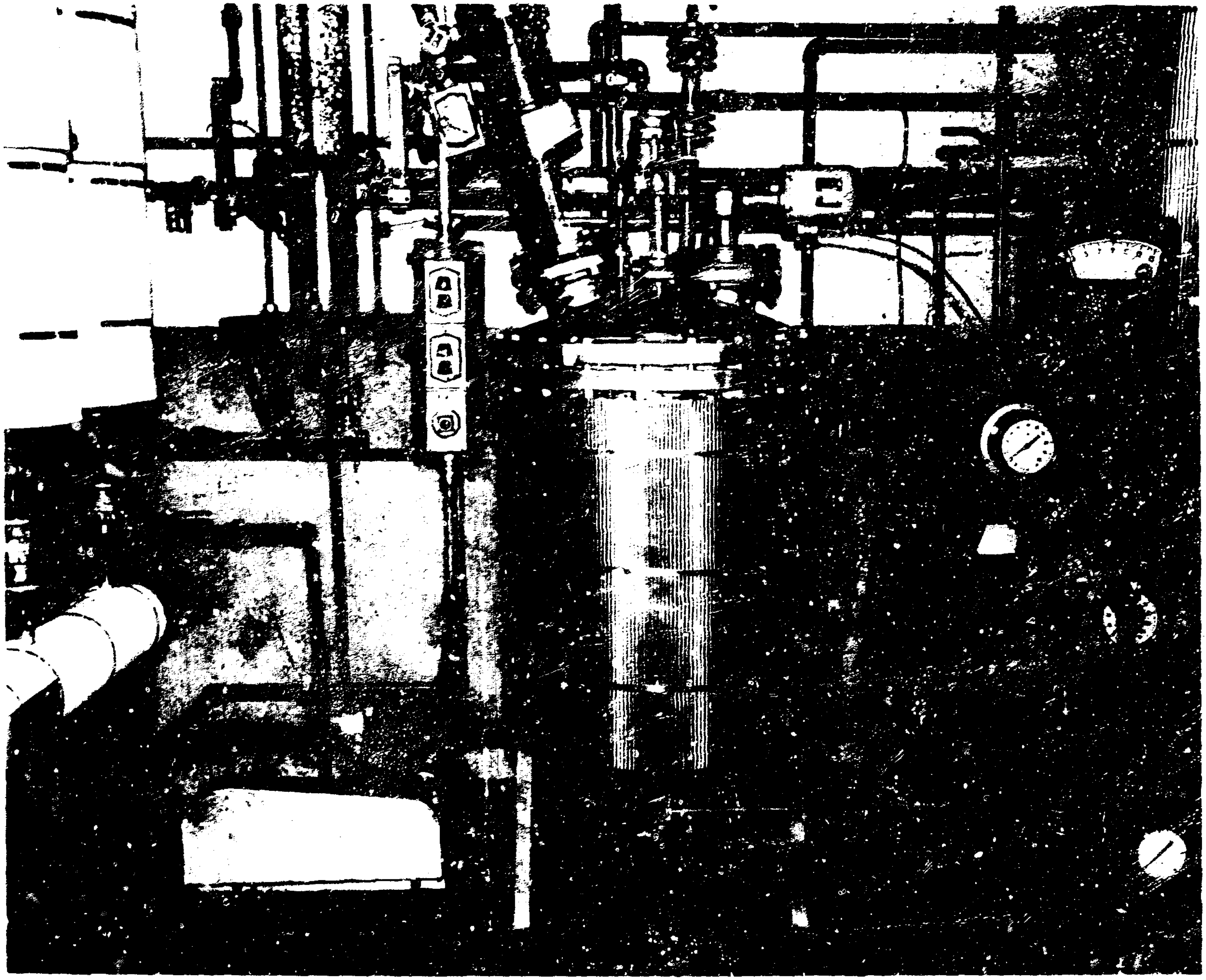

Figure II-6. Reactor Product Aqueous Quench Tank

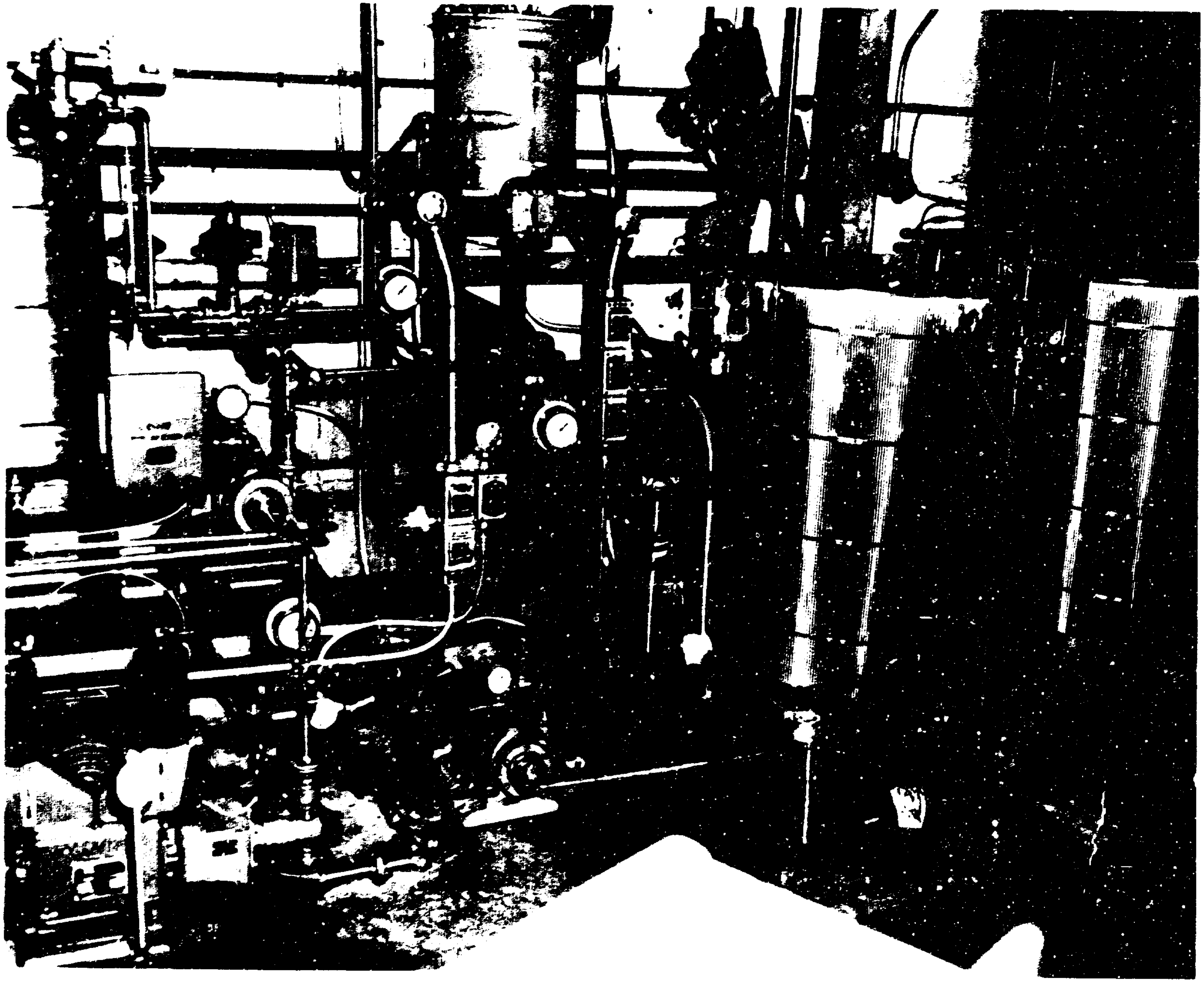

Figure II-7 [illegible] Separation/Crystallizer and Evaporator Hold Tanks

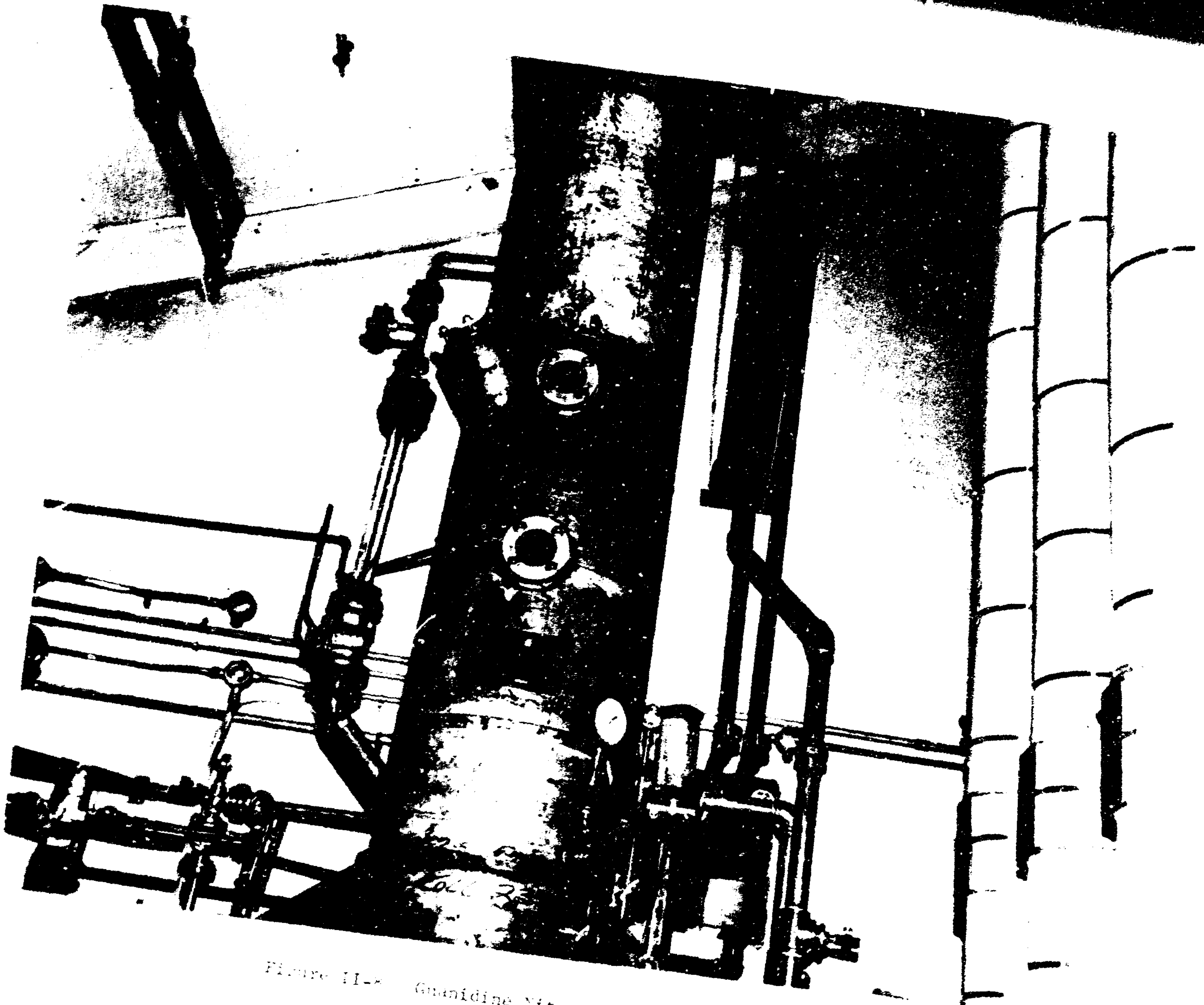

Figure II-[illegible] Guanidine Nitrate Vacuum Crystallizer

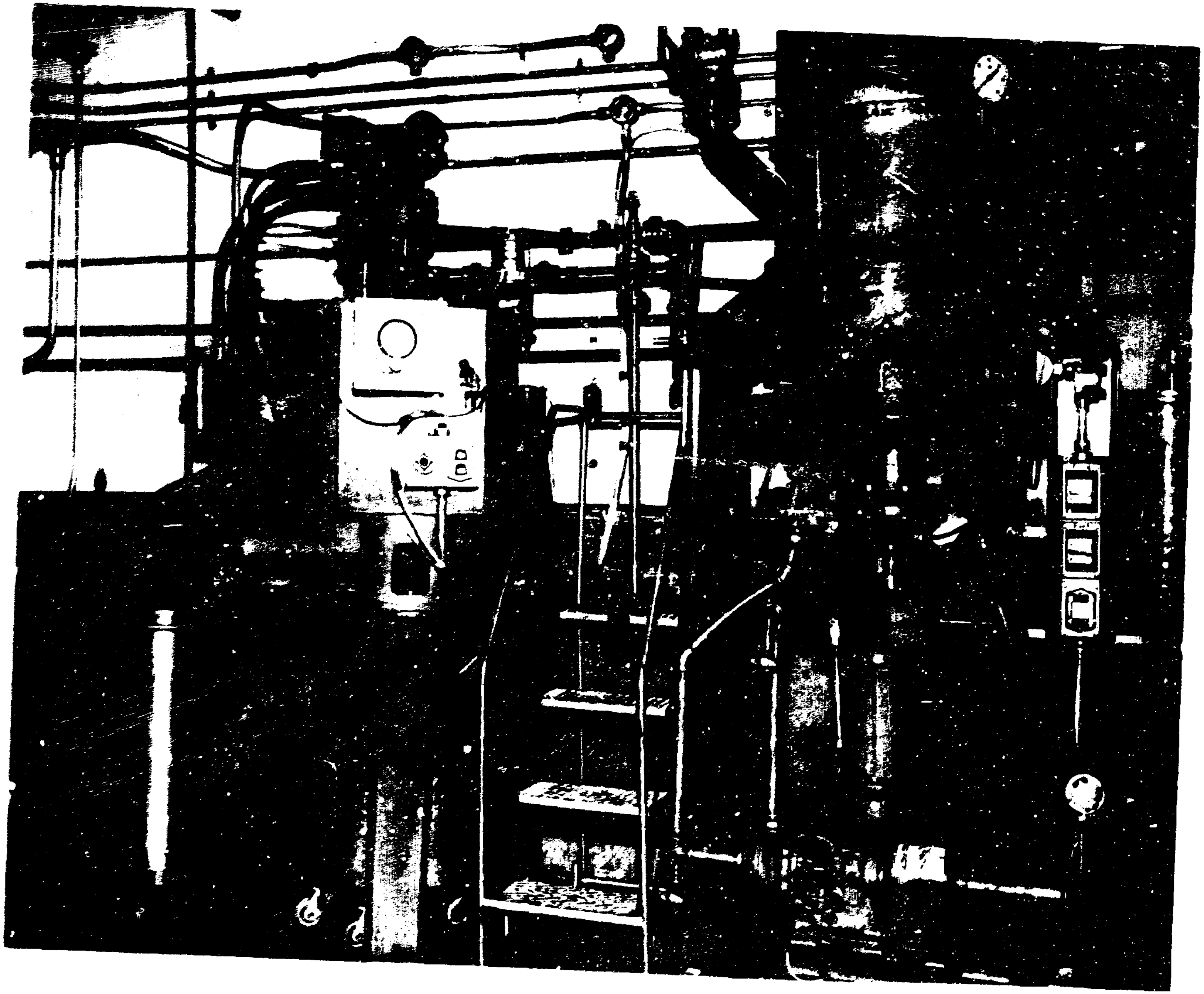

Figure II-[illegible] Guanidine Nitrate Crystallizer and Basket Centrifuge

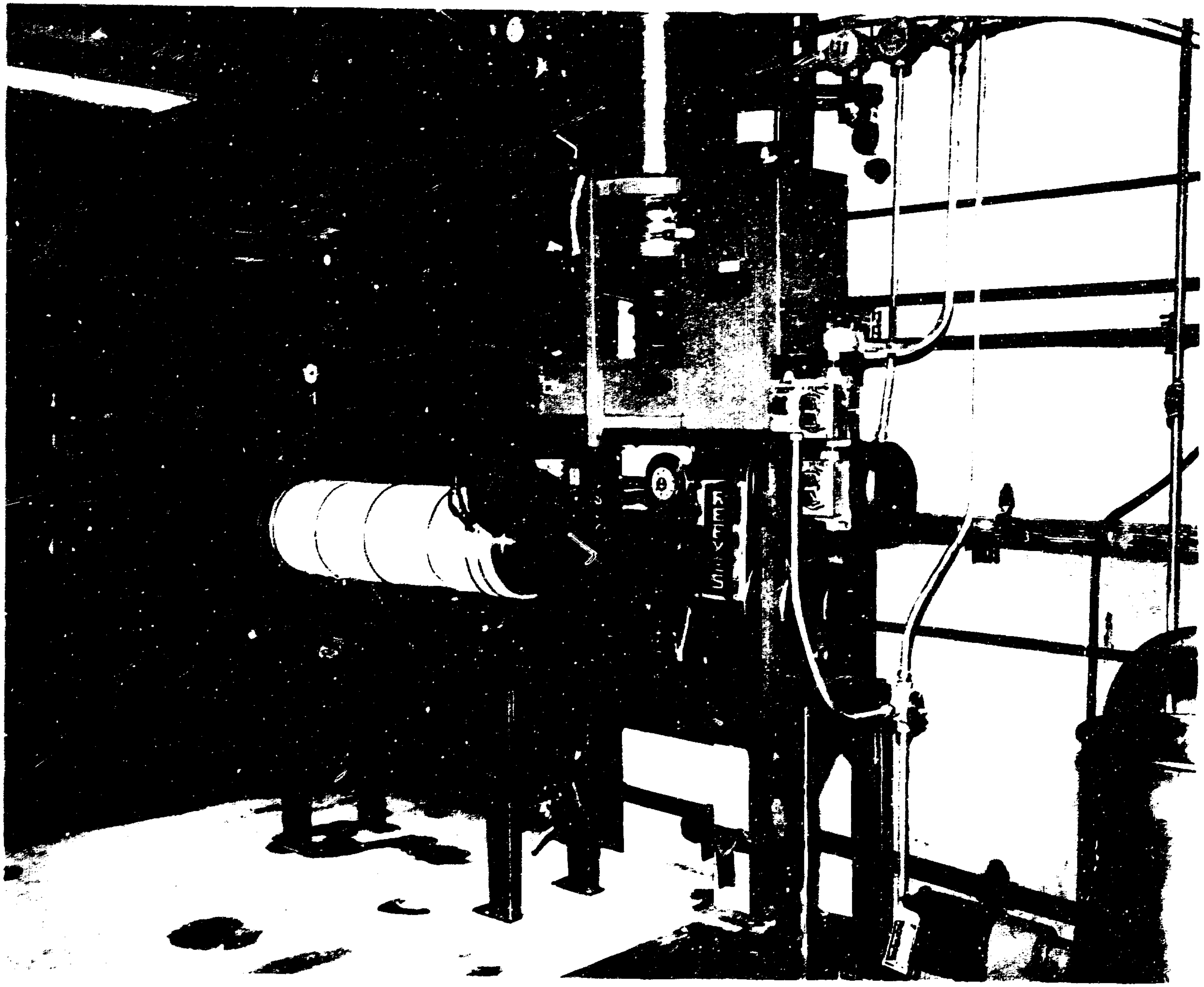

Figure II-10 Guanidine Nitrate Drying System

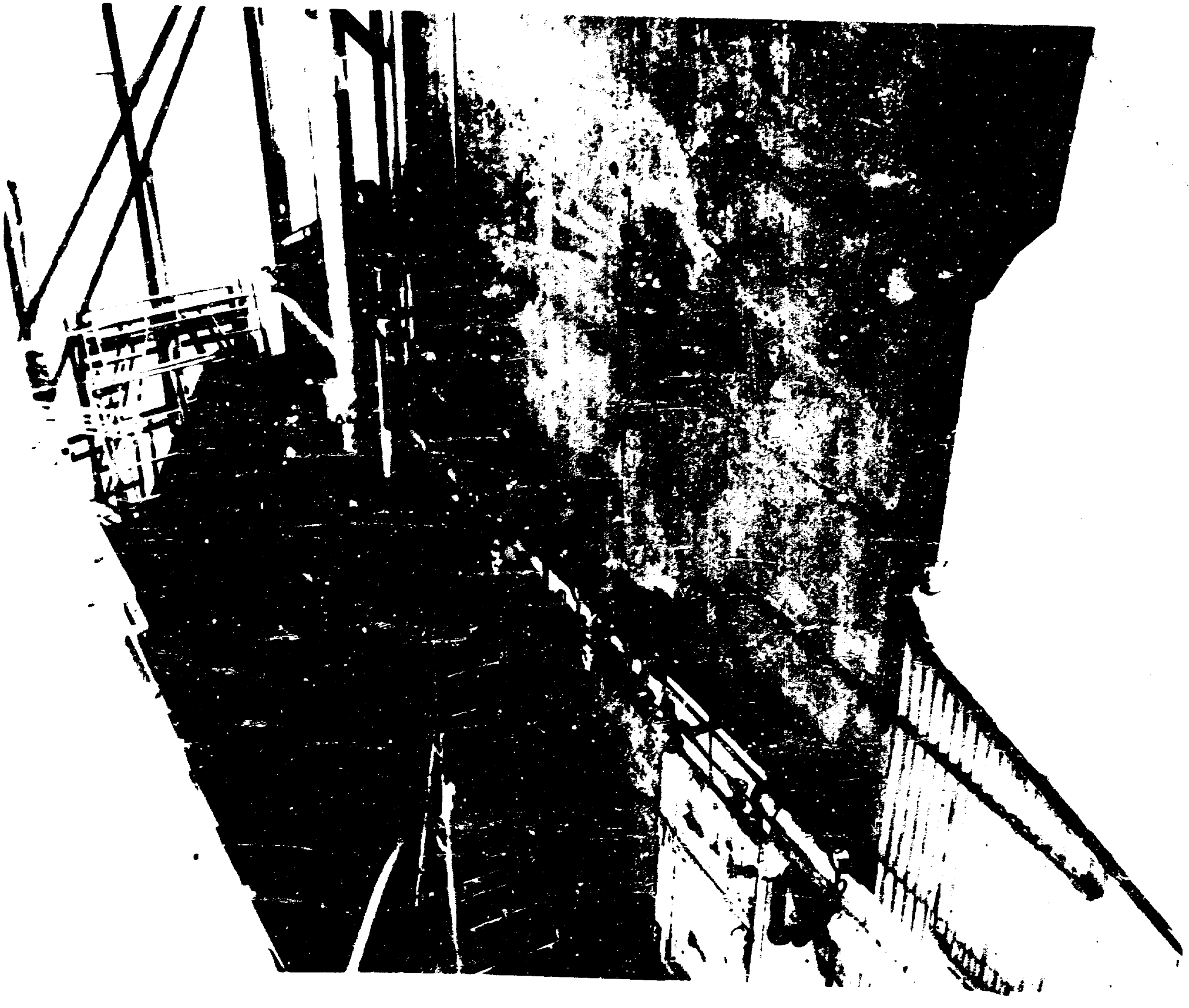

Figure II- [illegible] Building F1 - Evaporator for Reactor Feed Recycle

TABLE II-1

REACTOR PERFORMANCE
(Operating Conditions and Calculated Results)

Run No. 1 (6/8/72 → 6/29/72)

Date	6/8	6/13	6/14	6/15	6/15	6/16	6/21	6/21	6/21	6/21	6/21	6/21	6/22	6/22
Sample No. Calculations Based On	S1	S2	S1	S1	S2	S1	S1	S2	S3	S4	S5	S6	S1	S2
Time	0200	2020	0440	1620	2200	0400	0100	0400	0800	1300	1800	2015	0115	0660
Data														
Reactor Steam Pressure, psig	170	163	160	160	192	190	190	170/190	190	200	200	190	225	225
Effective No. of Tubes	2	3	2	2	4	2	3	1-3	3	2	1-2	2	1-2	1-2
% U, Feed/Product	28.7/ 16.9	41.5/ 25.6	39.8/ 29.3	28.7/ 20.6	28.2/ 14.3	56.1/ 40.0	43.4/ 19.6	42.6/ 25.3	43.1/ 24.7	36.7/ 22.5	39.3/ 21.0	34.8/ 24.3	45.2/ 24.5	44.9/ 24.9
% AN, Feed/Product	61.4/ 60.4	54.0/ 55.8	52.9/ 53.8	53.4/ 57.6	53.7/ 52.8	36.9/ 35.6	50.2/ 41.6	50.1/ 44.1	52.7/ 46.2	50.1/ 54.8	55.6/ 53.2	57.3/ 60.5	48.8/ 50.5	48.6/ 51.5
% GN, Feed/Product	8.0/ 22.0	1.4/ 13.9	6.2/ 11.1	11.3/ 14.6	12.7/ 31.1	3.2/ 12.9	5.5/ 35.1	3.5/ 27.8	4.8/ 24.6	4.2/ 22.1	2.4/ 14.9	6.0/ 13.7	5.8/ 20.0	2.9/ 14.9
% Insolubles, Product	0.35	Trace	0	0.4	1.3	0.25	0.19	0.62	0.41	0.29	0.15	0.19	0.3	0.24
Feed Rate, lb/hr	60	90	90	65	65	65	90	90	90	90	90	90	90	90
Calculations														
AN/U, Mole Ratio	1.6	0.98	1.[illegible]	1.[illegible]	1.43	0.9[illegible]	0.67	0.882	0.916	1.19	1.06	1.23	0.81	0.81
[illegible], Mole Basis	.417	0.232	[illegible]	[illegible]	0.419	0.2[illegible]	0.432	0.268	0.406	0.43	0.271	0.222	0.182	0.155
GN/lb Feed, Wt.	0.1156	0.1075	0.0414	0.015	0.1368	0.065	0.237	0.116	0.173	0.132	0.111	0.0605	0.0913	0.0836
Insolubles/GN, Wt.	0.027	-	-	0.247	0.081	0.0189	0.007	0.045	0.022	0.0173	0.0122	0.0275	0.026	0.0218
Plant Productivity, lb/hr	7	9.7	3.7	0.95	8.9	5	21.4	10.5	15.5	13.7	10.0	5.45	8.2	7.5

NOTES

Feeding to Reactors R204→7 (6/8 – 6/16)

Feeding Reactors R200→3 After Orifices in R204→7 Failed (6/21 – 6/22)

TABLE II-1 (Continued)

Date	[illegible]	6/22	6/23	6/23	6/23	6/27	6/27	6/27	6/28	6/28	6/28	6/28	6/29	6/29	6/29
Sample No., Calculations Based On	S[illegible]	S4	S1	S2	S3	S1	S2	S3	S1	S2	S3	S4	S1	S2	S3
Time	[illegible]	1630	0130	0530	0830	0400	0600	0800	0200	0700	1100	1400	0200	0600	1000
Data															
Reactor Steam Pressure, psig	[illegible]	22[illegible]	22[illegible]	22[illegible]	19[illegible]	190	190	200	190	195	190	194	190	190	190
Effective No. of Tubes	2-3	2-3	[illegible]	3	3	4	2	N.R.	4	3	3	3	2.5	4	2-3
% [illegible], Feed/Product	-	32.2/ 24.[illegible]	27.[illegible]/ [illegible].9	25.8/ [illegible].9	24.5/ 18.9	28.2/ 22.8	26.7/ 22.0	25.6/ 19.6	32.0/ 12.6	-/ 15.4	28.5/ 16.6	32.7/ 15.7	33.2/ 20.7	34.6/ 21.0	33.2/ 25.2
% AN, Feed/Product	-	[illegible]	[illegible]	[illegible]	61.1/ 61.5	58.6/ 57.6	60.5/ 58.9	61.6/ 60.8	57.2/ 49.9	-/ 56.1	61.0/ 61.6	55.5/ 64.3	57.9/ 60.8	57.5/ 59.2	62.3/ 63.7
% [illegible], Feed/Product	-	[illegible]/ 13.[illegible]	[illegible]	7.4/ [illegible]	8.5/ 21.7	10.[illegible]/ 16.9	10.3/ 17.8	9.7/ 17.3	6.6/ 37.6	-/ 27.3	4.9/ 21.5	6.7/ 18.9	4.6/ 17.0	3.4/ 16.3	1.4/ 9.1
% Insolubles, Product	-	[illegible]	0.33	0.38	0.26	0.17	0.33	0.31	0.89	0.63	0.79	0.58	0.55	0.69	0.32
Feed Rate, lb/hr	[illegible]	[illegible]	[illegible]	[illegible]	90	2[illegible]	2[illegible]	25	90	80	80	80	125	50	180
Calculations															
AN [illegible] Mole Ratio	-	[illegible]	[illegible]	1.8[illegible]	1.73	1.56	1.77	1.80	1.34	N/A	1.61	1.27	1.31	1.24	1.41
[illegible]	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.57	0.467	0.533	-	0.457	0.195	0.306	0.338	0.293
[illegible]	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.0665	0.234	-	0.133	0.08	0.0875	0.1055	0.0695
[illegible]	-	[illegible]	[illegible]	[illegible]	0.0219	[illegible]	0.0476	0.4[illegible]	0.0244	-	0.05	0.056	0.0478	0.0562	0.427
Plant Productivity, lb/hr	-	[illegible]	[illegible]	[illegible]	4.42	0.7	1.14	1.10	21.1	-	12.0	6.4	12.2	5.3	12.5

NOTES

Feeding Reactors [illegible], 201, 202, 203

Tried All Reactors; Problems With Flow Distribution, Boilers

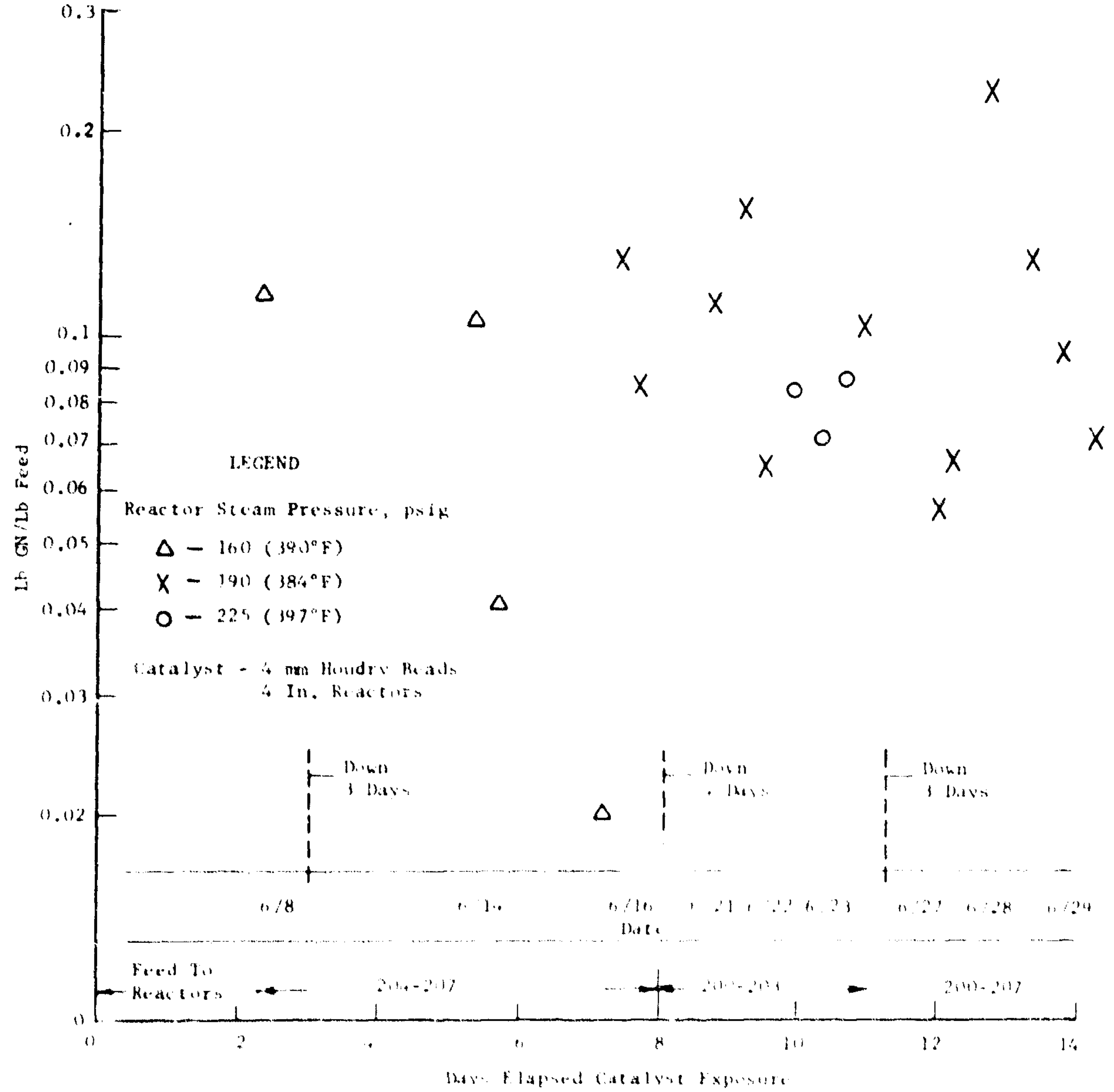

Figure II-12. Productivity Vs Time - First Catalyst Run

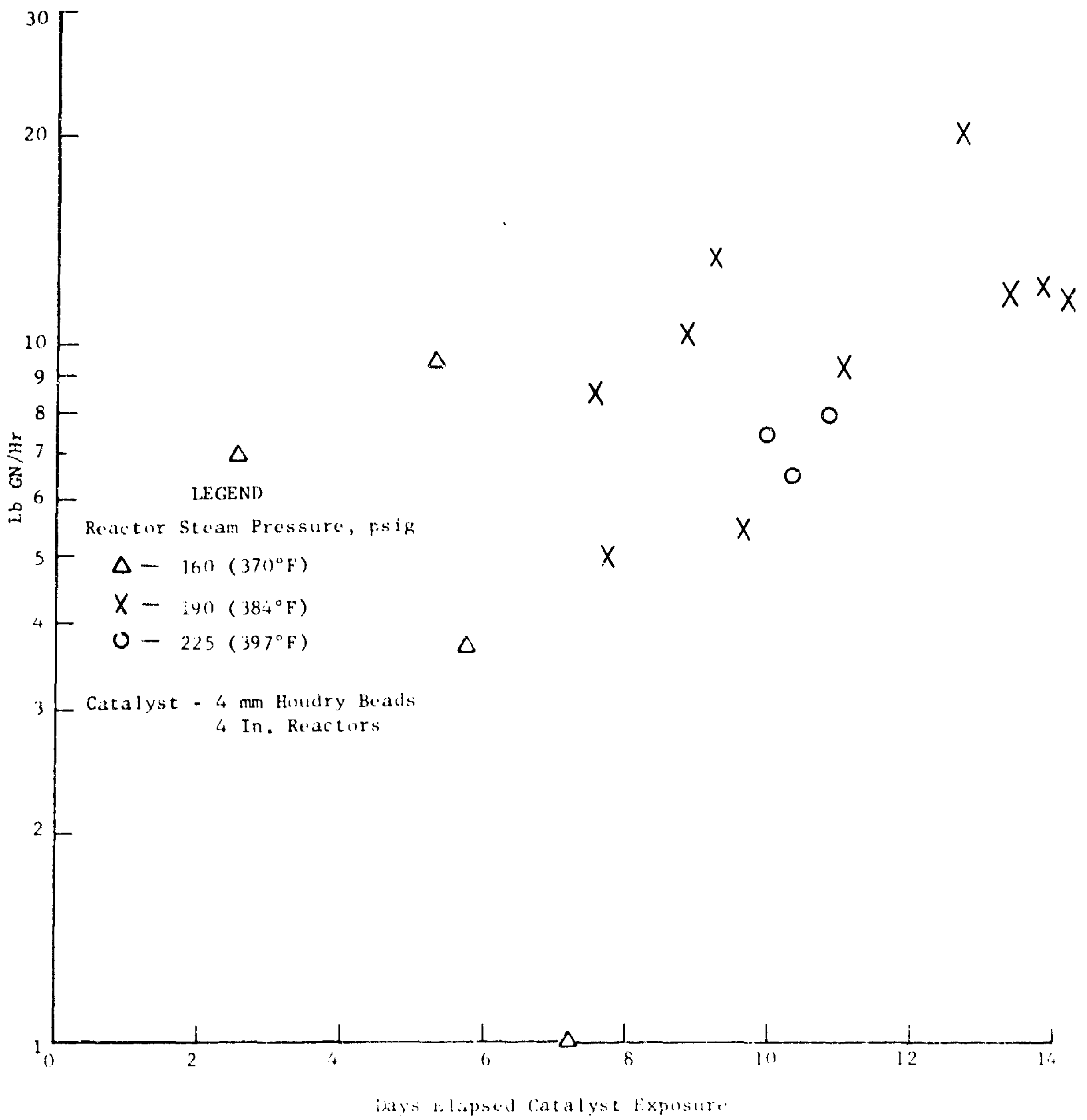

Figure II-13. Productivity/Hr Vs. Time - First Catalyst Run

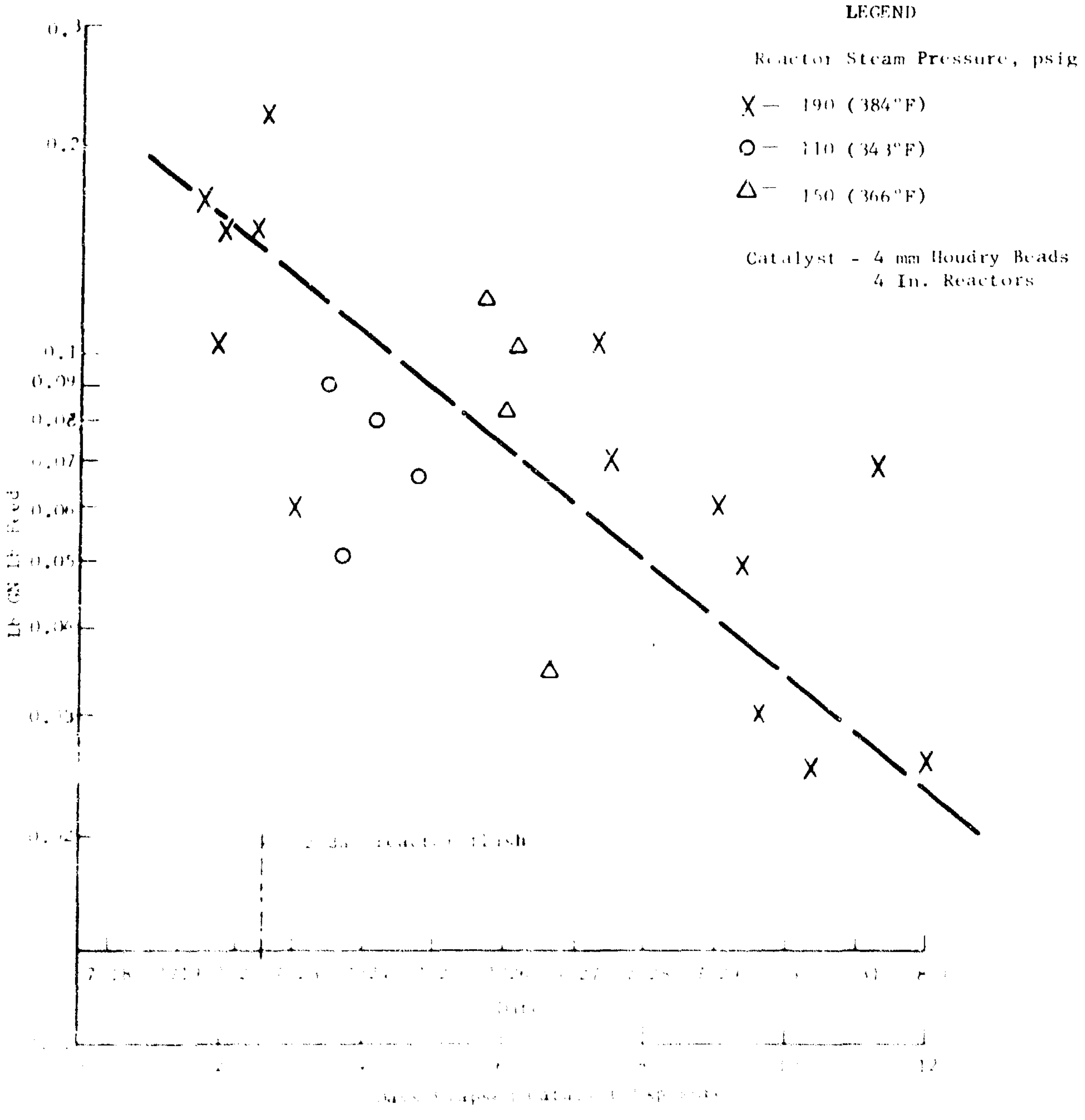

Figure II-14. Productivity Vs. Time - Second Catalyst Run

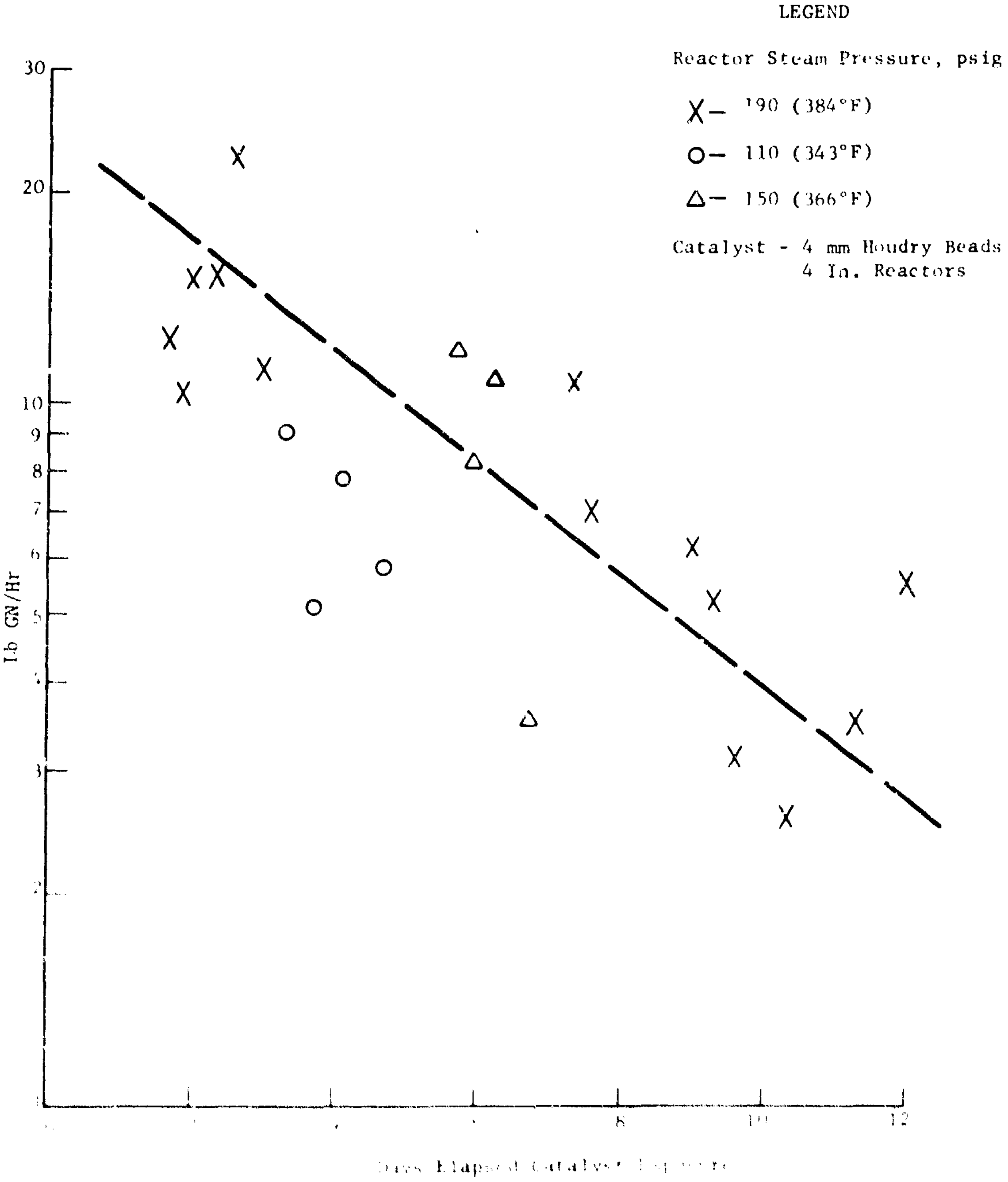

Figure II-15. Productivity/Hr Vs Time - Second Catalyst Run

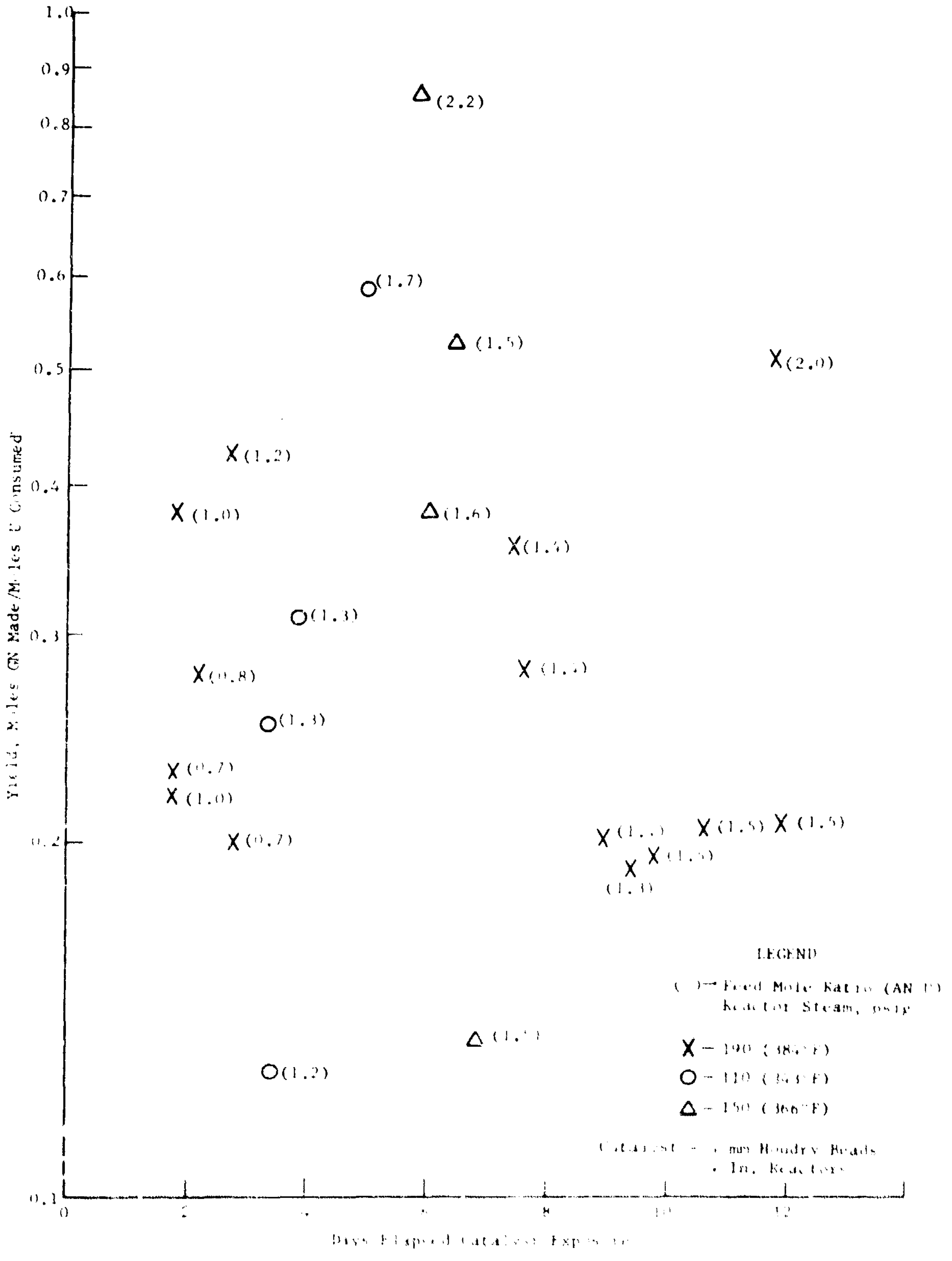

Figure II-16. Yield Vs Time - Second Catalyst Run

TABLE II-2

REACTOR PERFORMANCE
(Operating Conditions and Calculated Results)

Run No. 2 (7/19/72 → 8/1/72)

Date	7/19	7/19	7/19	7/20	7/20	7/20	7/21-7/22	7/23	7/23	7/23	7/24	7/24	7/24		7/25
Sample No., Calculations Based On	S1	S2	S3	S1	S2	S3	Programmed 75-125 psig; Reactor flush after suspected catalyst death. Startup at low feed temperature and reactor steam pressure.	S1	S3	S5	S1	S2	S3	7/24 - 2000 - Raised steam pressure to 150 psig (185°C)	S1
Time	[illegible]	[illegible]	[illegible]	0130		[illegible]		0300	1530	2330	0430	0830	1300		0030
Data															
Reactor Steam Pressure, psig	160	145	160	~ 190	~ 140	~ 190		110	110	115	110	100	110		150
Effective No. of Tubes	8	8	8	8	8	8		8	8	8	8	8	8		8
% [illegible] Feed/Product	[illegible]/ 13.[illegible]	[illegible]/ 20.2	[illegible].3/ 22.6	47.5/ 20.3	35.2/ 16.7	[illegible].8/ 29.4		33.7/ 19.5	34.9/ 19.6	33.3/ 23.4	-/ 33.7	-/ 27.2	27.4/ 24.6		-
% AN, Feed/Product	47.2/ 54.[illegible]	52.3/ 54.6	48.[illegible]/ 46.7	51.8/ 47.6	54.[illegible]/ 47.[illegible]	[illegible].3/ 51.9		58.4/ 63.7	56.8/ 63.3	59.0/ 60.5	-/ 61.2	-/ 61.0	60.4/ 61.6		-
% [illegible]N, Feed/Product	3.9/ 3[illegible].9	[illegible]/ 23.[illegible]	7.[illegible]/ 26.[illegible]	9.[illegible]/ 30.6	8.[illegible]/ 3[illegible].5	9.2/ 15.[illegible]		3.0/ 14.6	6.1/ 15.2	4.1/ 13.4	-/ 3.2	-/ 8.5	6.2/ 13.0		-
% [illegible], Product	[illegible].54	[illegible].82	[illegible]	[illegible].67	[illegible]	0.28		0.08	0.30	0.10	-	Trace	0.04		-
Feed Rate, lb/hr	75	[illegible]	1[illegible]	[illegible]	1[illegible]	175		100	100	100	100	100	100		100
Calculations															
AN/[illegible] Mole Ratio	.76	[illegible].95	[illegible].97	0.81	1.1[illegible]	0.73		1.30	1.13	1.32	-	-	1.65		1.84
[illegible]CN/AN [illegible], Mole Basis	.229	.223	.377	0.273	0.[illegible]28	0.194		0.251	0.121	0.311	-	-	0.598		-
[illegible](CN) Yield, Wt.	[illegible].1565	[illegible].315	[illegible].1563	0.1565	0.223	0.3631		0.909	0.0513	0.0788	-	-	0.0575		-
*Insolubles (GN) Wt.	.202	.0[illegible]4	[illegible].0056	0.035	0.[illegible]17	0.0285		0.0073	0.044	0.011	-	-	0.006		-
Plant Productivity, lb/hr	12.[illegible]	[illegible].3	[illegible]	15.6	22.3	11.1		9.0	5.1	7.9	-	-	5.8		-

NOTES:

Start July 17, New Catalyst; First Data 7/19, Flow to All Reactors

TABLE II-2 (Continued)

Date	7/25	7/25	7/25		7/26	7/26	7/26	7/26	7/26	7/27	7/27	7/27	7/27	7/27	7/28
Sample No. Calculations Based On	S2	S[illegible]	S4		S1	S2	S3	S4	-	S1	S2	S3	S4	S5	-
Time	[illegible]	1200	17[illegible]		0030	0530	0330	1300	1600	0130	04[illegible]	0830	1230	2000	1030
Data				Added Urea Prills to F-104 to Deplete System Accumulation - 4-12 Shift - 7/25					Changed Steam Pressure to 185 psig						Changed Makeup/Recycle Ratio From 15/85 → 25/75, Steam at 190 psig. Increased Feedrate to 105 lb/hr
Reactor Steam Pressure, psig	[illegible]	[illegible]	[illegible]		150	150	150	155		185	185	185	[illegible]	195	
Effective No. of Tubes	8	8	8		-	-	-	-		8	8	8	8	8	
% U, Feed/Product	24.8/	28.8/ 19.7	29.9/ 21.7		29.4/ 2.3	30.4/ 24.2	-	28.5/ 17.8		-	31.4/ 18.7	31.4/ 29.8	-	-	
% AN, Feed/Product	43.[illegible]/ 41.7	41.[illegible]/ 42.2	[illegible]/ [illegible]		57.7/ 59	56.7/ 58.7	-	56.9/ 61.5		-	58.3/ 60.0	58.3/ 57.9	-	-	
% GN, Feed/Product	[illegible]/ 4.7	7.2/ 17.1	[illegible].8/ 18.1		9.[illegible]/ 23.4	8.9/ 8.7	-	8.9/ 13.8			4.1/ 18.2	8.3/ 16.4	-	-	
% Insolubles, Product	[illegible].19	0.2[illegible]	0.32		0.32	-	-	-			0.40	0.25	-	-	
Feed Rate, lb/hr	[illegible]	[illegible]	[illegible]		100	100	[illegible]	100		100	100	100	100	100	
Calculations															
AN/U, Mole Ratio	[illegible]	[illegible]	2.[illegible]		1.47	1.[illegible]	-	1.49		-	1.40	1.40	-	-	
[illegible] Mol. basis	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	-	0.134		-	0.357	0.287	-	-	
% GN [illegible] Feed, Wt.	[illegible]	[illegible]	-		0.209	[illegible]	-	0.035		-	0.111	0.070	-	-	
Insolubles, GN, Wt.	[illegible]	[illegible]	-		0.0251	-	-	-		-	0.030	0.035	-	-	
Plant Productivity, lb/hr	12.3	8.3	-		10.9	[illegible]	-	3.3		-	11.1	7.0	-	-	

TABLE II-2 (Continued)

Date	7/28	7/28	7/28	7/29	7/29	7/29	7/30	7/30	7/30	7/30	7/31	7/31	7/31	7/31	8/1
Sample No. Calculations based On	S1	S2	S3	S1	S2	S3	Centrifuge Problems. Reduced Feed Rate to 50 lb/hr at 16<u>20</u> Stopped Fresh Feed at 17<u>30</u>	S1	S2	S3	S1	S2	S3	S4	Shut Down. Unable to Pump Through 5 of 8 Tubes
Time	0430	1130	2000	0400	1200	2000		0430	1200	2130	0430	1200	1630	2030	1500
Data															
Reactor Steam Pressure, psig	[illegible]	160	190	190	190	190		198	190	190	190	195	195	190	
Effective No. of Tubes	8	8	8	8	8	8		8	8	8	8	8	8	8	
% U, Feed/Product	-	-	30.9/ 19.3	31.4/ 20.8	29.5/ 22.1	-		-	28.9/ 23.6	-	22.8/ 17.4	-	-	28.4/ 23.1	
% AN, Feed/Product	-	-	57.1/ 60.6	56.1/ 60	58.9/ 58.1	-		-	59.4/ 58.6	-	62.0/ 60.3	-	-	58.5/ 60.6	
% GN, Feed/Product	-	-	6.6/ 15.1	8.8/ 15.7	11.0/ 14.4	-		-	8.8/ 17.5	-	9.7/ 17.6	-	-	4.0/ 7.9	
% Insolubles, Product	-	-	0.60	0.53	0.65	-		-	0.50	-	0.2	-	-	-	
Feed Rate, lb/hr	[illegible]	[illegible]	105	105	105	125		125	125	50	- 50	50	180	180	
Calculations															
AN/U, Mole Ratio	-	-	1.39	1.34	1.50	-		-	1.54	-	2.04	-	-	1.51	
[illegible], Mol. Basis	-	-	[illegible]	0.19	0.192	-		-	0.222	-	0.553	-	-	0.210	
% GN [illegible] Feed, Wt.	-	-	[illegible]	[illegible]	[illegible]	-		-	0.026	-	0.07	-	-	0.026	
Insolubles [illegible] Wt.	-	-	[illegible]	[illegible]	[illegible]	-		-	0.192	-	0.026	-	-	-	
Plant Productivity, lb/hr	-	-	6.36	5.3	3.2	-		-	2.62	-	3.5	-	-	5.6	

NOTES:

Boiler Problems

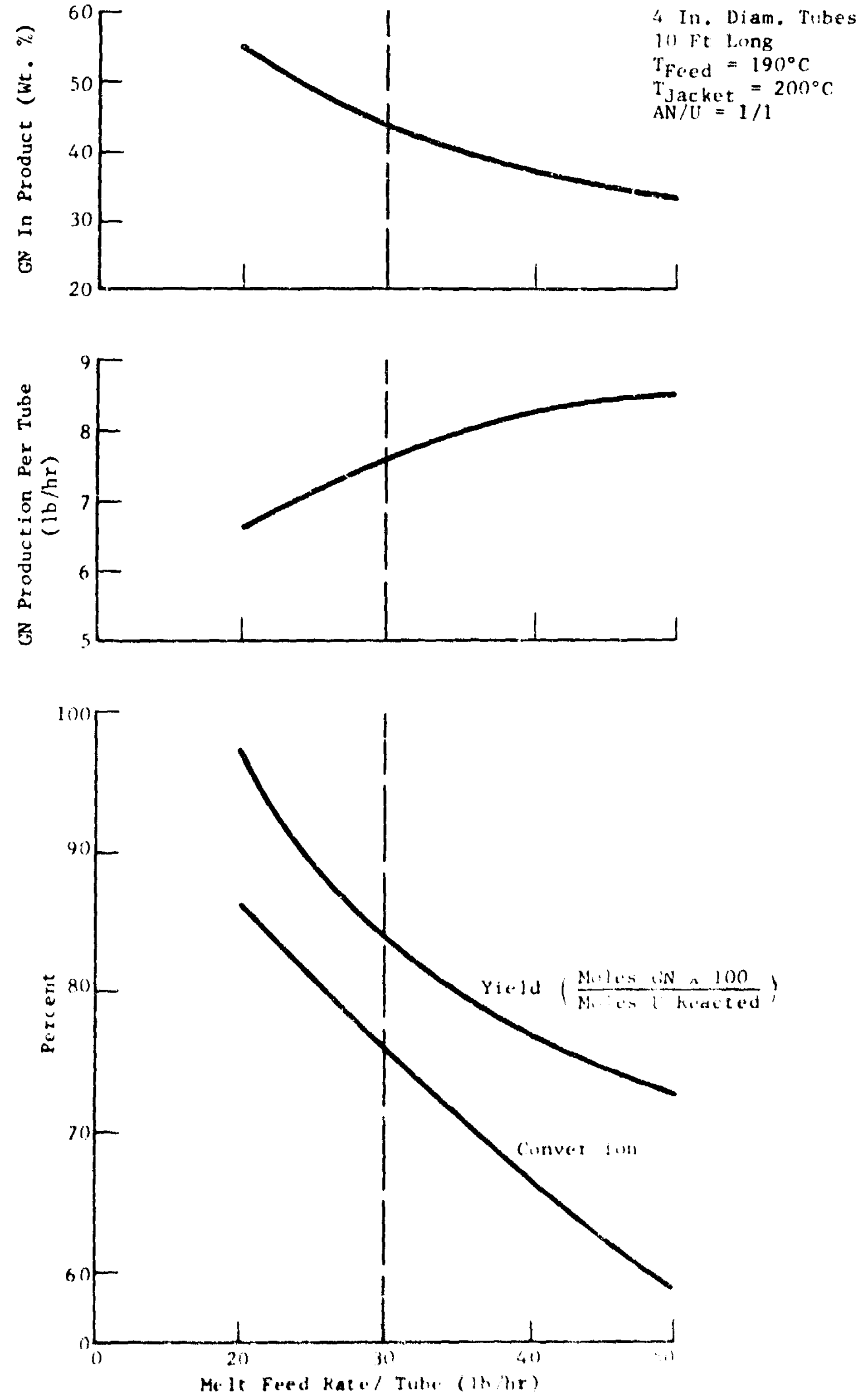

Figure II-17. Computer Prediction

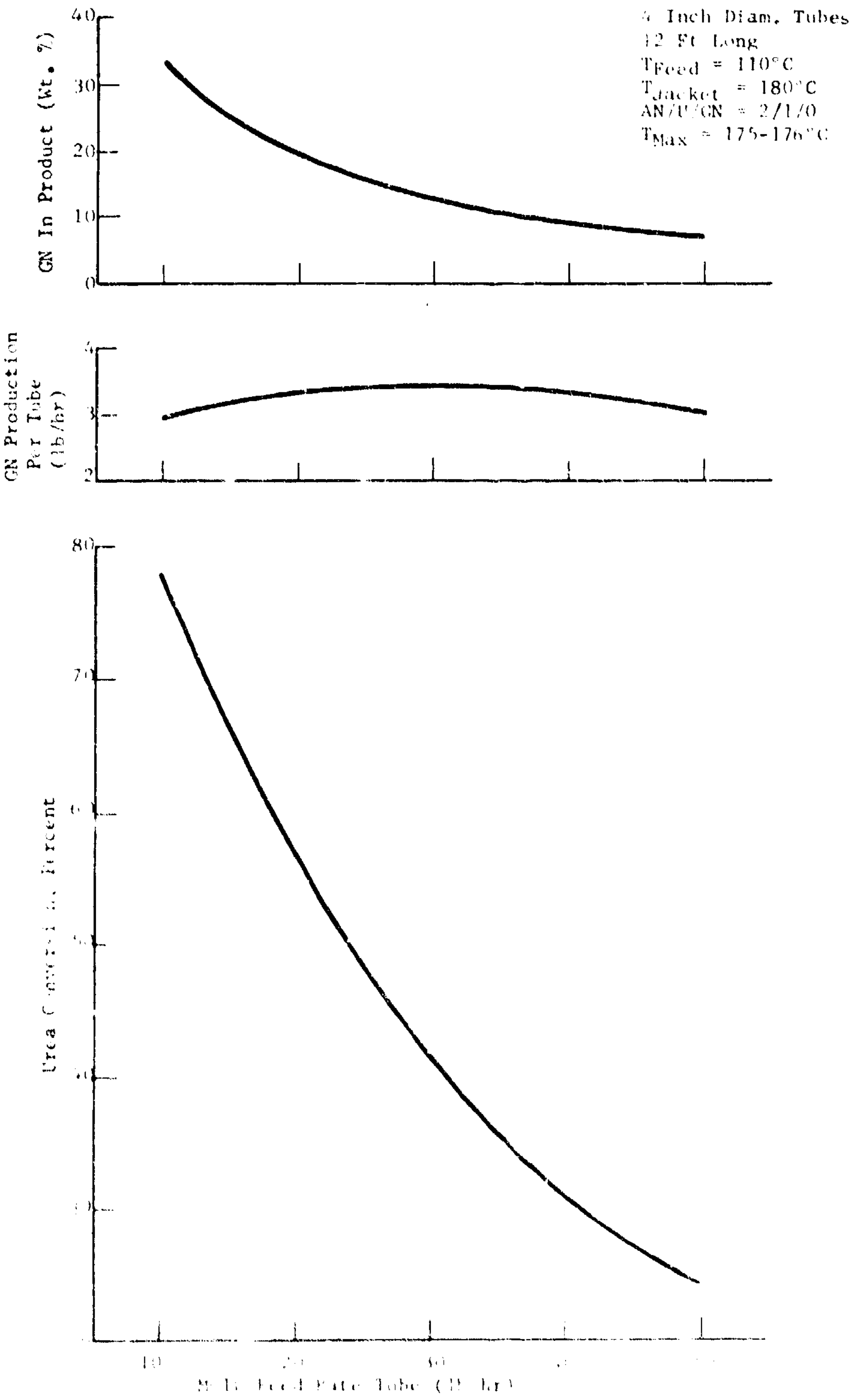

Figure II-18. Computer Prediction

TABLE II-3

SAMPLE CALCULATIONS FOR DETERMINING REACTOR YIELD AND PRODUCTIVITY

I Step by Step

Basis: Moles Nitrate are consumed.

$$2\ U + 1\ AN = 1\ GN + 2\ NH_3 + 1\ CO_2$$

(For every mole of AN consumed, one mole of guanidine nitrate is formed.)

Data: Reactor Steam Pressure = 225 psig

Feed Rate = 90 lb/hr

Analyses

	Feed			Product		
	%	Lbs. *	Moles **	%	Lbs. *	Moles **
Urea	25.8	25.8	.430	16.9	16.9	.282
Ammonium Nitrate	63.3	63.3	.791	62.4	62.4	.780
Guanidine Nitrate	7.4	7.4	.0606	18.4	18.4	.151
Insolubles	-	-	-	0.38	0.38	.003

* - Arbitrarily based on 100 lbs. of total material

** - Calculated moles based on arbitrary 100 lbs. material

Total Moles of Nitrate in Feed/100 lbs. Feed = Moles AN + Moles GN = 0.8516

Total Moles of Nitrate in Product/100 lbs. Product = 0.931

$$\frac{\text{Moles of Urea in Feed}}{\text{100 lbs. Feed}} \Big/ \frac{\text{Moles of Nitrate in Feed}}{\text{100 lbs. Feed}} = \left(\frac{\text{Moles Urea}}{\text{Moles Nitrate}}\right)_{\text{Feed}}$$

$$\left(\frac{U_M}{N}\right)_f = \frac{.430}{.8516} = .505$$

$$\frac{\text{Moles Urea in Product}}{\text{100 lbs. Product}} \Big/ \frac{\text{Moles of Total Nitrates in Product}}{\text{100 lbs. Product}} \left(\frac{\text{Moles Urea}}{\text{Moles Nitrate}}\right)_{\text{Product}}$$

$$\left(\frac{U_M}{N}\right)_P = \frac{.282}{.931} = .303$$

TABLE II-3 (Continued)

Similarily:

$$\left(\frac{GN_M}{N}\right)_{feed} = \frac{.0606}{.8516} = 0.0712 \qquad \left(\frac{GN_M}{N}\right)_{Product} = \frac{.151}{.931} = 0.162$$

$$\left(\frac{AM}{N}\right)_{feed} = 0 \qquad \left(\frac{AM}{N}\right)_{Product} = \frac{.003}{.931} = 0.0032$$

During the Reaction, then -

$$\Delta\left(\frac{U_M}{N}\right) = \left(\frac{U_M}{N}\right)_{Feed} - \left(\frac{U_M}{N}\right)_{Product} = 0.505 - 0.303 = 0.202$$

$$\Delta\left(\frac{GN_M}{N}\right) = \left(\frac{GN_M}{N}\right)_{Feed} - \left(\frac{GN_M}{N}\right)_{Product} = 0.0712 - 0.162 = -0.091$$

Or a loss of 0.202 moles urea per nitrate mole and a gain of 0.091 moles GN per nitrate mole.

<u>Feed Mole Ratio</u> $\left(\frac{AN_M}{U_M}\right)_{Feed} = 0.791/0/430 = 1.84$

<u>Yield</u>

<u>Basis:</u> $2\ U + 1\ AN \quad 1\ GN + 2\ NH_3 + 1\ CO_2$

or 2 moles U consumed per mole of GN made.

$$\text{Yield} = \frac{\text{Moles GN made}}{\text{Moles U consumed}/2} \times 100$$

$$= \frac{GN_M}{U_M} \times 200 = \frac{\left(\frac{GN_M}{N}\right)}{\left(\frac{U_M}{N}\right)} \times 200$$

$$\text{Yield} = \frac{0.091}{0.202} \times 200 = 89.9\%$$

<u>Productivity</u>

Productivity/lb. Feed = lbs. GN Made/lb. Feed

$$= \left(\frac{\text{Moles GN Made}}{\text{Moles Total Nitrate}}\right) \times \frac{\text{Moles Nitrate in Feed}}{\text{100 lbs. Feed}} \times \text{M. W.}_{GN}$$

TABLE II-3 (Continued)

$$\text{Productivity/lb. Feed} = \frac{\Delta GN_M}{N} \times \frac{N_{Feed}}{100} \times 122 =$$

$$0.091 \times 0.8516 \times 1.22$$

$$\underline{\text{Productivity/lb. Feed} = \text{Lbs. GN Made/Lb. Feed} = 0.0945}$$

Plant Productivity

$$\text{Plant Productivity} = \text{Lbs. GN Made/Hour}$$

$$= \frac{\text{Lbs. GN Made}}{\text{Lb. Feed}} \times \text{Lbs. Feed /Hr.}$$

$$= 0.0945 \times 90 \text{ lbs. /hr.}$$

$$\underline{\text{Plant Productivity} = 8.5 \text{ lbs. /hr.}}$$

Insolubles Formation

$$\text{Insolubles Productivity} = \frac{\Delta AM}{N} \times \frac{N_{Feed}}{100 \text{ lbs. Feed}} \times \text{M. W. X Feed Rate}$$

$$= 0.0032 \times 0.8516 \times 1.28 \times 90 \text{ lb/hr}$$

$$= 0.314 \text{ lbs/hr.}$$

Productivity Insolubles/Guanidine Nitrate = 0.314/8.5 = 0.037

TABLE II-3 (Continued)

II. Alternative Calculation Procedure

Nomenclature

X_j	total weight			
x_{ij}	weight fraction			
y_{ij}	moles			
i	1 = feed		2 = liquid output	
j	1	2	3	4
COMPOUND	GN	AN	U	INSOLUBLES
Mw	122	80	60	UNKNOWN

1. $y_{ij} = X_j \, x_{ij} / Mw_j$

2. $y_{11} + y_{12} = \left[\frac{x_{11}}{Mw_1} + \frac{x_{12}}{Mw_2}\right] X_1 = \left[\frac{x_{21}}{Mw_1} + \frac{x_{22}}{Mw_2}\right] X_2 = y_{21} + y_{22}$

3. $X_1 = \beta X_2$

Where: $\beta = \frac{x_{11} + x_{12}\, Mw_1/Mw_2}{x_{21} + x_{22}\, Mw_1/Mw_2} = \frac{x_{11} + 1.525\, x_{12}}{x_{21} + 1.525\, x_{22}}$

$$\text{Yield} = \frac{-200\,(x_{11} - x_{21}\beta)/Mw_1}{(x_{13} - x_{23}\beta)/Mw_3} = \frac{-98.36\,(x_{11} - x_{21}\beta)}{x_{13} - x_{23}\beta}$$

GN PRODUCTIVITY RATE = $(x_{11} - x_{21}\beta)\,\dot{X}_1$

INSOLUBLE FORMATION RATE = $x_{24}\,\beta\,\dot{X}_1$ $\quad (x_{14} = 0)$

INSOLUBLE PRODUCT RATIO = $-\frac{x_{24}}{x_{11}/\beta + x_{21}}$ $\quad (x_{14} = 0)$

TABLE II-3 (Continued)

Sample Calculations (using data from prior method)

1. $$\beta = \frac{x_{11} + 1.525\,x_{12}}{x_{21} + 1.525\,x_{22}} = \frac{.074 + 1.525(.633)}{.184 + 1.525(.624)} = .9152$$

2. $$Y = \frac{-98.36\,(x_{11} - x_{21}\beta)}{x_{13} - x_{23}\,\beta} = \frac{-98.36(.074 - .184(.9152))}{.258 - .169(.9152)} = 89.9\%$$

3. GN PRODUCTIVITY RATE $= (x_{11} - x_{21}\beta)\,\dot{X}_1$

From (2), $(x_{11} - x_{21}\beta) = .0944$

$\therefore$ GN $= .0944\,(90) = 8.5\ ^{LBS}/_{HR}$

4. INSOLUBLE FORMATION RATE $= x_{24}\,\beta\,\dot{X}_1 = .0038(.9152)(90) = .313\,\frac{LBS}{HR}$

5. RATIO $$= -\frac{x_{24}}{x_{11}/\beta + x_{21}} = \frac{-.0038}{.074/.9152 - .184} = .0369$$

APPENDIX III

PHASE III, PART 2

RESOLUTION OF CATALYST POISONING PROBLEM

TABLE III-1

DETAILED DATA FOR HOUDRY BEAD ACTIVITY AND SORBEAD® STIRRED BATCH EXPERIMENTS

Catalyst	Run No.	Charge Wts. (gm) AN	U	Cat	Total	React Temp. (°C)	Sample Time (hr)	Analytical Results Wt. % AN	U	CN	[illegible]	Wt. Insolubles	[illegible] Sample	Final Melt	[illegible]	Misc.	Total	Mat'l. Balance (%)	Final Reactor Melt (gm)	Moles U Reacted	Moles CN Formed	CN Yield (%)	U Conv. (%)	Moles Carbonate/ Moles CN	gm CN/ gm Catalyst
New Houdry Beads	42-0	260	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	1.585	0.6322	79.8	57.8	-	0.504
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2.32	0.9162	70.7	67.3	0.932	0.731
New Houdry Beads	43-0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	43-1	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	[illegible]	[illegible]	0.4265	73.2	38.8	-	0.310
	43-4	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	[illegible]	[illegible]	0.4963	81.7	40.5	-	0.315
	43-5	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	1.307	0.5381	82.3	43.6	[illegible]	0.429
Used Houdry Beads Top B-20C	44-0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	[illegible]	-	-	1.0(2)	0.17
Used Houdry Beads Top B-20C	45-0	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	0.127	-	-	1.0(2)	0.10
Used Houdry Beads Water Washed Top B-20C	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	0.3270	0.2112	128	0.165	-	0.261
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.9721	0.2528	52	0.486	1.11	0.312
New Sorbead R Beads	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.6386	654	[illegible]	1.28	0.507
Used Houdry Top Reactor	48-0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	0.182	-	-	1.0(2)	0.145
New Sorbead [illegible] Beads	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	[illegible]	[illegible]	108	39.2	-	0.505
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	[illegible]	[illegible]	51	52.6	-	0.321
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	71	65.6	[illegible]	0.557
[illegible] Washed Top Reactors (Used Houdry Beads)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	-22	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	[illegible]	[illegible]	59.1	33.6	-	0.345
	-23	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.1554	46.7	44.3	1.05	0.360
Alc-[illegible] Washed Top (Used Houdry Beads)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	[illegible]	0.2294	55.8	41.1	-	0.241
	[illegible]	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	0.9669	0.3288				0.344

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(1) IR spectrum abnormal.

(2) Ratio of 1.0 assumed.

TABLE III-2

DETAILED DATA FOR GRACE 59 SILICA GEL

Catalyst	Run No.	Charge Wts. (gm)				React. Temp ([illegible])	Sample Time ([illegible])	Analytical Results Wt. %				% Insolubles	Weights Out (gm)					Mat'l. Balance (Wt. % Loss)	Final Reactor Melt (gm)	Moles U Reacted	Moles GN Formed	GN Yield (%)	U Conv. (%)	Moles Carbonate/ Moles GN	gm GN/ gm Cat.
		AM	U	Cat.	Total			AM	U	GN	Closure		Sample	Remaining Mix	Carbon-ate	Misc.	Total								
Grace Grade 59 Silica Gel	52-0	26[illegible]	180	153	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	-26	-	-	-	-	[illegible]	12[illegible]	[illegible]	25.[illegible]	15.3	6.0	5[illegible].1	1[illegible]	-	-	-	-	-	-	1.480	0.4514	61.0	49.3	-	0.360
	-27		-	-		[illegible]	[illegible]	[illegible]	18.0	[illegible]	6.3	[illegible]	[illegible]	-	-	-	-	-	-	1.953	0.3095	72.7	65.1	-	0.366
	-28	-	-	-	-	[illegible]	[illegible]	(Not Enough Liquid Left To Sample)					[illegible]	-	-	-	-	-	-	-	-	-	-	-	-
		2[illegible]	180	-	99[illegible]	[illegible]	[illegible]	(Another Charge of U and AM Added to the Reactor, Silica Gel Remained in the Reactor)																	
	-29	-		-		[illegible]	[illegible]	[illegible]	29.1	27.8	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	[illegible].792	1.564	82.5	63.2	-	1.25
	-30			-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2[illegible]	[illegible]	-	-	-	-	-	-	4.346	1.859	85.5	72.4	-	1.46
	-31		-	-	-	[illegible]	[illegible]	[illegible]	8.1	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	8.2	948.2	4.5	590.9	5.148	2.303	89.[illegible]	85.8	0.809	1.84
Grace Grade 59 Silica Gel, Recov'd U-AM [illegible] after Heat Aging for 6 Hr @ [illegible]	53-0	26	180	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-	-	-
	-32		-	-	-	[illegible]		[illegible]	27.7	-	7.1	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-
	33	-	-	-	-	[illegible]	12.[illegible]	[illegible]	25.6	12.5	5.8	[illegible]	[illegible]	-	-	-	-	-	-	1.576	0.3709	47.1	52.5	-	0.276
	-34			-	-	[illegible]	[illegible]	[illegible]	[illegible]	23.[illegible]	2.3	[illegible]	[illegible]	-	-	-	-	-	-	2.106	0.637	60.4	70.2	-	0.507
Fresh Recov'd U and AM Used for Second Charge		2[illegible]	180	-	99[illegible]	-	[illegible]	(Another Charge of U and AM Added, [illegible])						-	[illegible]	-									
	35		-			[illegible]	[illegible]	[illegible]	28.[illegible]	9.[illegible]	[illegible].9	9[illegible]	[illegible]	-	-	-	-	-	-	2.431	0.599	49.3	40.5	-	0.477
	36		-	-		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	3.406	0.979	57.5	56.8	-	0.781
	37		-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7.6	[illegible]	[illegible]	[illegible]	13[illegible]	6.5	996.5	0.68	662.3	3.73	1.063	57.0	62.2	1.63	0.847
Grace Grade 59 Silica Gel, Recov'd U and AM	[illegible]	[illegible]	[illegible]	[illegible]	99[illegible]	[illegible]		-	-	-	-	-		-	-	-	-	-	-	-	-	-	-	-	-
	39		-	-		[illegible]	[illegible]	[illegible]	28.[illegible]	[illegible]	89.[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	3.22	0.0[illegible]84	2.6	37.8	-	0.046
	[illegible]		-	-		[illegible]	[illegible]	[illegible]	14.6	[illegible]	68.[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	3.53	0.736	41.7	58.8	-	0.586
	[illegible]		-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	9[illegible]	[illegible]	[illegible]	823.[illegible]	[illegible]	[illegible]	976.3	[illegible].7	682.8	[illegible].53	[illegible].654	37.1	58.8	2.23	0.521
Grace Grade 59 Silica Gel, Recov'd [illegible] and AM	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]					[illegible]	[illegible]	[illegible]	29.[illegible]	[illegible]	9[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	2.321	[illegible]	40.9	38.3	-	0.375
	[illegible]						[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	-	-	-	-	-	-	2.775	[illegible]	46.9	46.9	-	0.522
	[illegible]					[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	-	-	3.8[illegible]	1.[illegible]	67.1	63.5	-	1.02
	[illegible]					[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	99.[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	970.2	2.3	626.9	4.425	1.[illegible]13	77.4	73.8	1.04	1.37
Grace 59 With [illegible] Urea and Reagent AM	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		-	-	-	-			-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]					[illegible]			[illegible]	[illegible]	8[illegible]			-	-	-	-	-	-	2.2[illegible]	0.[illegible]10	36.4	37.5	-	0.327
	[illegible]					[illegible]			[illegible]	[illegible]	9[illegible]		[illegible]	-	-	-	-	-	-	3.28	0.844	53.[illegible]	52.9	-	0.623
	[illegible]					[illegible]	[illegible]	[illegible]	[illegible]	28.[illegible]	[illegible]		[illegible]	-	-	-	-	-	-	4.1[illegible]	1.623	76.5	69.2	-	1.30
	[illegible]					[illegible]	[illegible]		[illegible]	38.[illegible]	[illegible]		[illegible]	[illegible].7	[illegible]	[illegible]	94[illegible]	3.1	61[illegible].8	4.66	2.0[illegible]	86.1	77.8	0.929	1.60
Grace [illegible] With [illegible] AM and [illegible] Urea		[illegible]	[illegible]		[illegible]	[illegible]																			
						[illegible]			[illegible]	[illegible]	[illegible]			-	-	-	-	-	-	-	-	-	-	-	-
	[illegible]					[illegible]	[illegible]		[illegible]	[illegible]	9[illegible]			-	-	-		-	-	[illegible]	[illegible]	[illegible].2	37.0	-	[illegible]
	[illegible]					[illegible]	[illegible]		[illegible]	[illegible]	[illegible]		[illegible]	-	-	-			-	[illegible]	[illegible]	57.8	44.6	-	[illegible].616
	[illegible]					[illegible]	[illegible]		[illegible]	[illegible]	9[illegible]			[illegible]	[illegible]	[illegible]	94[illegible]	[illegible]	64[illegible]	[illegible]	1.[illegible]62	75.3	74.5	1.14	1.34

TABLE III-3

LABORATORY BEAKER TESTS

Run #1 - X2121-36-1

Procedure - Added 10-15 grams dry silica gel (Grade grade 59) to 275 grams of molten AN/U at 300°F. (2/1 AN/U mole ratio)

- Hand stirred for ten minutes
- Allowed catalyst to settle
- Poured off melt
- Spread wet silica gel on paper towel.
- * (Dried at 165°F overnight)

Observations -

- Bubbling on first contact presumably due to venting of entrained air.
- Wet silica gel on paper towel was very soft. It fractured with the slightest touch.
- Estimated attrition was 5-10%.

Run #2 - X2121-37-1

Procedure - Same as X2121-36-1 except melt contained 5% liquid water.

Observations - Same as Run #1 but with a higher percentage of attrition (10-20%).

Run #3 - X2121-37-2

Procedure - Dropped dry silica gel (Grace grade 59) into boiling water (212°F).

- Stirred for ten minutes
- Allowed catalyst to settle
- Poured off water
- Spread wet silica gel on paper towel.

Observations -

- Bubbling on first contact presumably due to venting of entrained air.
- Wet silica gel was softer than the dry silica gel but much harder than recovered catalyst from Runs #1 and #2.
- Estimated attrition was less (5%) than in the two previous runs.

TABLE III-3 (Continued)

Run #4 - X2121-38-1

Procedure - Dropped dry Houdry beads into a melt of AN/U as in Run #1.

Observations -

- Houdry beads floated on top of the melt for about five minutes before sinking. After sinking, the beads continued to release vented air for an additional 5-10 minutes.

- Recovered beads appeared to be harder than the original beads. There was no apparent catalyst attrition.

Run #5 - X2121-39-1

Procedure - Same as Run #1 but using preheated silica gel (350-400°F)

Observations - Same conclusions as noted for Run #3.

TABLE III-4

FOUR-INCH-DIAMETER REACTOR SUMMARY (a)

Basis
1. [illegible] Reactor (R-200
2. Houdry Macroporous Silica Beads
3. Hercules' Donora Reagent Grade AN, Olin C
4. Recycle - None

	1-29-73 7:30 P.M. 3			1-29-73 10:30 P.M. 6			1-30-73 1:00 A.M. 8.5			1-30-73 1:00 P.M. 9.5			1-30-73 4:30 P.M. 13		
	Feed		Reactor	Feed		Reactor	Feed		Reactor	Feed		Reactor	Feed		Reactor
1. [illegible] 2. [illegible] 3. [illegible] Time (hrs)	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt
4. [illegible]	30	30	-	30	30	-	Feed stopped 1:00 AM - 12:00 Noon due to plant steam failure (melters, feed line, etc.) Reactor drained and high steam pressure maintained on reactor jacket.			35	35	-	35	35	-
5. [illegible]															
a. [illegible]	28.4	27.3	9.9	26.2	27.3	8.5				-	27.3	7.6	-	27.3	4.4
b. AN	69.4	72.7	67.4	71.7	72.7	65.5					72.7	68.5		72.7	68.1
c. CN	3.1	-	23.4	2.2	-	26.9					-	23.7		-	28.2
d. H_2O	0.6		-	0.5		-									-
e. Insolubles	-			-											
6. [illegible]	0.474	0.455	0.165	0.437	0.455	0.141					0.455	0.126		0.455	0.073
7. AN	0.866	0.909	0.842	0.896	0.909	0.816					0.909	0.856		0.909	0.852
8. CNm	0.025	-	0.192	0.018	-	0.220					-	0.194		-	0.231
9. [illegible]	0.891	0.909	1.034	0.914	0.909	1.036					0.909	1.050		0.909	1.083
10. [illegible]	0.531	0.498	0.160	0.479	0.498	0.136					0.498	0.120		0.498	0.067
11. [illegible]	0.028	-	0.186	0.020	-	0.212					-	0.185		-	0.213
	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed
12. [illegible]	0.371		0.338	0.345		0.362						0.378			0.431
13. [illegible]	0.158		0.156	0.191		0.212						0.185			0.213
14. [illegible]	0.425		0.550	0.540		0.575						0.490			0.495
15. [illegible]	85.0		110.0	102.0		115.0						98.0			99.0
16. [illegible] (1.22)	0.172		0.206	0.213		0.235						0.205			0.236
17. [illegible] CN [illegible] Rate)	5.16		6.2	6.4		7.1						7.2			8.3

TABLE III-4 (Continued)

(b)

Basis:
1. One Reactor (R-200
2. Houdry Macroporous Silica Beads
3. Hercules' Donora Reagent Grade AN, Olin U
4. Recycle - None

1. Date	1-30-73			1-30-73			1-31-73			1-31-73			1-31-73		
2. Time	7:30 P.M.			10:30 P.M.			1:30 A.M.			4:30 A.M.			7:30 A.M.		
3. Elapsed Feed Time (hrs)	16			19			22			25			28		
	Feed		Reactor	Feed		Reactor	Feed		Reactor	Feed		Reactor	Feed		Reactor
	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt
4. Rate (lbs/hr.)	35	35	-	35	35	-	35	35	-	35	35	-	35	35	-
5. Analysis (%)															
a. U	22.0	27.3	4.4		27.3	5.9	-	27.3	4.7	-	27.3	5.4	26.7	27.3	6.0
b. AN	75.2	72.7	69.7		72.7	70.1		72.7	69.6		72.7	70.2	69.7	72.7	65.0
c. GN	3.4	-	26.9		-	24.8		-	26.2		-	24.8	2.4	-	29.4
d. H_2O	0.5					-			-			-	0.5		-
e. Insolubles	-												-		0.01
6. Um.	0.367	0.455	0.073		0.455	0.098		0.455	0.078		0.455	0.090	0.445	0.455	0.100
7. ANm.	0.940	0.909	0.872		0.909	0.878		0.909	0.872		0.909	0.877	0.872	0.909	0.818
8. GNm	0.028	-	0.220		-	0.208		-	0.214		-	0.203	0.019	-	0.241
9. Nm.	0.968	0.909	1.092		0.909	1.081		0.909	1.086		0.909	1.080	0.891	0.909	1.059
10. Um/Nm.	0.379	0.498	0.067		0.498	0.096		0.498	0.072		0.498	0.083	0.499	0.498	0.092
11. GNm/Nm	0.029	-	0.202		-	0.188		-	0.197		-	0.188	0.021	-	0.228
	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed
12. ΔU/N	0.312		0.431			0.402			0.426			0.415	0.407		0.406
13. ΔGN/N	0.173		0.202			0.188			0.197			0.188	0.207		0.228
14. ΔGN/N° (ΔU/N)	0.555		0.470			0.466			0.462			0.453	0.509		0.561
15. Yield (%)	111.0		94.0			93.2			92.4			90.6	101.8		112.2
16. Productivity (lb. GN/lb. Feed) (ΔGN/N)(N Feed) (1.22)	0.204		0.223			0.208			0.218			0.208	0.225		0.253
17. Production (lb. GN/hr.) (Productivity × Feed Rate)	7.1		7.8			7.26			7.6			7.3	7.9		8.9

TABLE III-4 (Continued)

(c)

Basis:
1. One Reactor (R-200
2. Houdry Macroporous Silica Beads
3. Hercules' Donora Reagent Grade AN, Olin U
4. Recycle - None

1. Date	1-31-73			1-31-73			1-31-73			1-31-73			1-31-73		
2. Time	10:00 A.M.			1:00 P.M.			4:00 P.M.			7:00 P.M.			11:00 P.M.		
3. [illegible] Feed Time (hrs)	30.5			33.5			36.5			39.5			43.5		
	Feed		Reactor	Feed		Reactor	Feed		Reactor	Feed		Reactor	Feed		Reactor
	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt
4. Rate (lbs/hr.)	34	34	-	28	28	-	25	25	-	28	28		25	25	
5. Analysis (%)															
a. [illegible]	28.6	27.3	5.1	-	27.3	5.0	-	27.3	4.8		27.3	5.5	24.7	27.3	5.0
b. AN	67.9	72.7	63.7		72.7	61.4		72.7	65.5		72.7	67.8	71.3	72.7	69.3
c. GN	3.3	-	32.0		-	32.7			30.8			27.9	3.4	-	27.1
d. H_2O	0.8		-			-			-		-	-	0.8		-
c. Insolubles	-												-		0.05
6. [illegible]	0.477	0.455	0.085		0.455	0.083		0.455	0.080		0.455	0.092	0.412	0.455	0.083
7. ANm	0.849	0.909	0.797		0.909	0.767		0.909	0.819		0.909	0 848	0.891	0.909	0.866
8. GNm	0.027	-	0.262		-	0.268		-	0.252		-	0 228	0.028	-	0.222
[illegible]	0.876	0.909	1.059		0.909	1.035		0.909	1.071		0.909	1 076	0.919	0.909	1.088
[illegible]	0.545	0.498	0.083		0.498	0.080		0.498	0.070		0.498	0 085	0.455	0.498	0.076
[illegible]	0.031	=	0.248		-	0.258		-	0.236			0.212	0.035	-	0.204
	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed
[illegible]	0.462		0.415			0.418			0.428			0.413	0.379		0.422
[illegible]	0.217		0.248			0.258			0.236			0.212	0.169		0.204
[illegible]	0.470		0.598			0.617			0.551			0.514	0.445		0.484
[illegible]	94.0		117.6			123.4			110.2			102.8	89.0		96.8
[illegible]	0.232		0.274			0.286			0.262			0.235	0.189		0.226
[illegible] Ratio	7.9		9.33			8.0			6.8			6.6	4.7		5.7

TABLE III-4 (Continued)

(d)

Basis:
1. One Reactor (R-200
2. Houdry Macroporous Silica Beads
3. Hercules' Donora Reagent Grade AN, Olin U
4. Recycle - None

1. Date	2-1-73			2-1-73			2-1-73			2-2-73			2-2-73		
2. Time	1:00 A.M.			7:30 P.M.			10:30 P.M.			1:30 A.M.			4:30 A.M.		
3. Elapsed Feed Time (hrs)	45.5			48			51			54			57		
	Feed		Reactor	Feed		Reactor	Feed		Reactor	Feed		Reactor	Feed		Reactor
	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt	Actual	Theo.	Melt
4. Rate [illegible]	System down 1:00 AM 2-1-73 until 5:00 PM 2-1-73 due to plant steam shortage. On startup, changed from 2/1 to 1/1 (N/U) ratio.			27	27		27	27	18	27	27	-	25	25	17
5. Analysis [illegible]					*						*				
a. U				36.9	42.9	4.8	36.9	42.9	5.2	36.9	42.9	8.3	40.6	42.9	6.8
b. AN				59.2	57.1	65.4	59.2	51.1	57.1	59.2	57.1	60.3	55.3	57.1	45.8
c. GN				3.0	-	31.8	3.0	-	33.3	3.0	-	30.0	2.2	-	45.5
d. H_2O				1.1		-	1.1		-	1.1		-	-	-	-
e. Insolubles				-			-			-					0.270
6. [illegible]				0.615	0.715	0.080	0.615	0.715	0.087	0.615	0.715	0.138	0.677	0.715	0.113
7. [illegible]				0.740	0.715	0.818	0.740	0.715	0.713	0.740	0.715	0.754	0.691	0.715	0.573
GNm				0.025	-	0.261	0.025	-	0.318	0.025	-	0.246	0.018	-	0.372
[illegible]				0.765	0.715	1.079	0.765	0.715	1.031	0.765	0.715	1.000	0.709	0.715	0.945
[illegible]				0.805	1.000	0.074	0.805	1.000	0.084	0.805	1.000	0.138	0.958	1.000	0.120
[illegible]				0.033	-	0.242	0.033	-	0.309	0.033	-	0.246	0.025	-	0.394
	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed
[illegible]				0.731		0.926	0.721		0.916	0.667		0.862	0.838		0.880
[illegible]				0.209		0.242	0.276		0.309	0.213		0.246	0.369		0.394
[illegible]				0.286		0.261	0.382		0.337	0.320		0.286	0.440		0.448
[illegible]				57.2		52.2	76.4		67.4	64.0		57.2	88.0		89.6
[illegible] (1.22)				0.195		0.228	0.258		0.294	0.198		0.214	0.318		0.344
[illegible]				5.3		6.2	7.0		8.0	5.4		5.8	8.0		8.6

* Used 10:30 P.M., 2/1/73 feed analysis

TABLE III-4 (Continued)

(e)

Basis:
1. One Reactor (R-200
2. Houdry Macroporous Silica Beads
3. Hercules' Donora Reagent Grade AN, Olin U
4. Recycle - None

	Feed Actual	Feed Theo.	Reactor Melt	Feed Actual	Feed Theo.	Reactor Melt	Feed Actual	Feed Theo.	Reactor Melt	Feed Actual	Feed Theo.	Reactor Melt	Feed Actual	Feed Theo.	Reactor Melt
1. Date	2-2-73			2-2-73			2-2-73			2-2-73			2-2-73		
2. Time	7:30 A. M.			10:30 A.M.			1:30 P.M.			7:30 P.M.			10:30 P.M.		
3. Elapsed Feed Time (hrs)	60			63			66			72			75		
4. Rate (lbs/hr.)	29	29		30	30	29	30	30	27	30	30	27	27.5	27.5	21
5. Analysis (%)															
a. U	-	42.9	6.8	-	42.9	9.3	-	42.9	9.9	40.0	42.9	14.4	40.0	42.9	9.6
b. AN		57.1	44.1		57.1	44.5		57.1	45.0	55.3	57.1	45.9	55.4	57.1	44.6
c. GN		-	51.2		-	45.7			43.6	2.4	-	39.5	4.7	-	46.4
d. H₂O			-			-			-	1.5		-	1.5		-
e. Insolubles			0.350							-			-		
6. Um		0.715	0.113		0.715	0.155		0.715	0.165	0.667	0.715	0.260	0.667	0.715	0.160
7. ANm		0.715	0.552		0.715	0.556		0.715	0.562	0.691	0.715	0.574	0.693	0.715	0.558
8. GNm		-	0.420		-	0.375		-	0.357	0.020	-	0.324	0.039	-	0.380
9. Nm		0.715	0.972		0.715	0.931		0.715	0.919	0.711	0.715	0.898	0.732	0.715	0.938
10. Um/Nm		1.000	0.116		1.000	0.166		1.000	0.179	0.938	1.000	0.289	0.910	1.000	0.171
11. GNm/Nm		-	0.432		-	0.402		-	0.389	0.028	-	0.361	0.053	-	0.405
	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed
[illegible]	-		0.884	-		0.834	-		0.821	0.649		0.711	0.739		0.629
[illegible]			0.432			0.402			0.389	0.333		0.361	0.352		0.403
[illegible]			0.489			0.483			0.473	0.515		0.507	0.476		0.487
[illegible]			97.8			96.6			94.6	103.0		101.4	95.2		97.4
[illegible] (1.22)			0.377			0.351			0.338	0.289		0.309	0.314		0.352
[illegible] GN hr [illegible] Feed Rate)			10.4			10.5			10.2	8.7		9.3	8.7		9.7

TABLE III-4 (Continued)

(f)

Basis:
1. One Reactor (R-200)
2. Houdry Macroporous Silica Beads
3. Hercules' Donora Reagent Grade AN, Olin C
4. Recycle - None

1. Date	2-3-73			2-3-73			2-3-73			2-3-73			2-3-73		
2. Time	4:30 A.M.			7:30 A.M.			10:30 A.M.			4:30 P.M.			10:30 P.M.		
3. Elapsed Feed Time (hrs)	81			84			87			93			99		
	Feed		Reactor Melt	Feed		Reactor Melt	Feed		Reactor Melt	Feed		Reactor Melt	Feed		Reactor Melt
	Actual	Theo.		Actual	Theo.		Actual	Theo.		Actual	Theo.		Actual	Theo.	
4. [illegible]	28.5	28.5	17	28.5	28.5	18	26.5	26.5	18	27.5	27.5	19	26.5	26.5	18
5. [illegible]															
a. [illegible]	-	42.9	11.3	-	42.9	9.8	39.6	42.9	8.9	41.4	42.9	10.1	-	42.9	10.7
b. AN		57.1	44.1		57.1	40.9	56.3	57.1	45.7	54.8	57.1	44.9		57.1	43.9
c. [illegible]		-	43.7		-	48.7	2.7	-	45.6	4.0	-	45.5		-	44.5
d. [illegible]			-			-	1.0		-	1.4		-			-
e. Insolubles						0.390	-								
6. [illegible]		0.715	0.189		0.715	0.163	0.660	0.715	0.148	0.690	0.715	0.168		0.715	0.178
7. [illegible]		0.715	0.551		0.715	0.511	0.704	0.715	0.571	0.685	0.715	0.561		0.715	0.549
8. [illegible]		-	0.358		-	0.400	0.022	-	0.374	0.015	-	0.373		-	0.365
9. [illegible]		0.715	0.909		0.715	0.911	0.726	0.715	0.945	0.700	0.715	0.934		0.715	0.914
10. [illegible]		1.000	0.208		1.000	0.179	0.909	1.000	0.156	0.986	1.000	0.180		1.000	0.195
11. [illegible]		-	0.394		-	0.439	0.030	-	0.396	0.021	-	0.399		-	0.400
	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed
[illegible]			0.792			0.821	0.743		0.344	0.806		0.320	-		0.805
[illegible]			0.394			0.439	0.366		0.396	0.378		0.399			0.400
[illegible]			0.497			0.533	0.492		0.470	0.469		[illegible]			0.497
[illegible]			[illegible]			100.6	98.4		94.6	93.8		[illegible]			[illegible]
[illegible]			[illegible]			0.382	[illegible]		0.349	0.322		0.348			0.348
[illegible]			[illegible]			[illegible]	5.6		9.1	6.9		8.6			9.2

TABLE III-4 (Continued)

(g)

Basis:
1. One Reactor (R-200
2. Houdry Macroporous Silica Beads
3. Hercules' Donora Reagent Grade AN, Olin U
4. Recycle - None

	Feed Actual	Feed Theo.	Reactor Melt	Feed Actual	Feed Theo.	Reactor Melt	Feed Actual	Feed Theo.	Reactor Melt	Feed Actual	Feed Theo.	Reactor Melt	Feed Actual	Feed Theo.	Reactor Melt
[illegible]	2-4-73			2-4-73			2-4-73			2-4-73					
[illegible]	1:30 A. M.			7:30 A. M.			10:30 A. M.			2,30 P. M.					
[illegible] Feed Time (hrs)	102			108			111			115					
[illegible]	25	25	14	27	27	16	27	27	24	26	26	21			
[illegible]													RUN VOLUNTARILY TERMINATED 2:30 P.M. 2-4-73		
[illegible]		42.9	9.8	37.7	42.9	7.5	39.5	42.9	7.7		42.9	8.6			
[illegible]		57.1	43.4	57.9	57.1	47.4	57.4	57.1	46.0		57.1	46.4			
CN			46.3	2.7	-	45.0	4.5	-	46.9		-	44.9			
Hg			-	0.9		-	1.2		-			-			
e. Insolubles							-		0.490						
[illegible]		0.715	0.163	0.628	0.715	0.125	0.658	0.715	0.128		0.715	0.143			
ANm		0.715	0.542	0.724	0.715	0.592	0.718	0.715	0.575		0.715	0.580			
CNm		-	0.379	0.022	-	0.368	0.039	-	0.384		-	0.368			
[illegible]		0.715	0.921	0.766	0.715	0.960	0.757	0.715	0.959		0.715	0.948			
[illegible]		1.000	0.177	0.820	1.000	0.130	0.870	1.000	0.134		1.000	0.151			
[illegible]		-	0.411	0.029	-	0.383	0.052	-	0.400		-	0.388			
	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed	Calc. Basis Actual Feed		Calc. Basis Theo. Feed
[illegible]			0.623	[illegible]		0.870	0.736		0.866			0.849			
[illegible]			0.412	0.254		0.383	0.348		0.400			0.388			
[illegible]			0.590	0.51		0.440	0.472		0.462			0.457			
[illegible]			[illegible]	[illegible]		[illegible]	94.4		92.4			91.4			
[illegible]			[illegible]	[illegible]		[illegible]	0.321		0.348			0.338			
[illegible]			[illegible]	[illegible]		[illegible]	[illegible]		[illegible]			8.8			

APPENDIX IV

HAZARD EVALUATION AND RISK CONTROL FOR KENVIL GUANIDINE NITRATE

(Reprint of Summary Report)

This is a final summary report on the work completed during Phases I through III of the Hazards Evaluation and Risk Control on the Kenvil pilot plant for the production of guanidine nitrate via the Boatwright-McKay-Roberts (BMR) process.

Objectives

Phase I

1. Assure safety of bench scale operations.

2. Secure basic sensitivity data (initiation, transition, propagation) for pilot plant design, for engineering analysis and pilot plant Fault Tree Analysis.

3. Construct preliminary Logic Model (Fault Tree) of the pilot plant.

4. Coordinate safety data with engineering design.

Phase II

1. Perform a preliminary engineering analysis on equipment chosen for pilot plant operation with regard to potential hazards and safety margin.

2. Determine transition capability of the reactor mixture in a 4 inch by 12 foot reaction tube.

3. Refine logic model for simulation.

Phase III

1. Final engineering analysis of selected pilot plant equipment.

2. Perform a risk analysis of the pilot plant operation and conduct trade-off design modifications should an unacceptable risk be encountered.

Summary and Conclusions

Data from sensitivity tests indicate that materials in the pilot plant process are relatively insensitive to impact, friction, ESD and thermal stimuli.

It has been determined that no material in the pilot plant equipment will transit from burning to explosion. In other words, the pilot plant system is not capable of acting as an explosive shock donor to process materials.

Two materials (reaction mixture and guanidine nitrate) will propagate an explosive reaction if sufficiently boostered. The critical diameter for each is less than one inch. Other materials in the pilot plant will not sustain an explosive reaction in the one inch interconnecting pipelines.

A detailed engineering analysis of selected pilot plant equipment for possible hazards and safety margins has shown no hazards for normal operating conditions. Abnormal occurrences; such as, metal/metal contact between impellers and pump cases or mix blades and tanks would cause initiation. However, transition data show that only a fire would result.

Computer simulation of the logic model (Fault Tree) yielded 152 potential initiation modes, 21 of which were considered to be critical or most probable of occurring. The simulation was performed over 800 hours of operation with no maintenance or repair and resulted in a probability of initiation of 4.6×10^{-3} or a corresponding probability of no initiation of 0.9953. This is an acceptable risk (initiation only) since the losses due to initiation during operation of the pilot plant would be minimal when compared to the cost of reducing the probability of initiation by (1) scheduled maintenance, (2) replacement of designated equipment on a regular basis, or (3) redesign of equipment. However, if the presently designed pilot plant were to be scaled up to a production plant operating over a span of years where any downtime or interruption of the process would have a significant effect on the safety, cost and productivity of the facility, a recommendation for scheduled maintenance, repair or redesign might be warranted.

DISCUSSION

Material Sensitivity

Initiation testing of materials was completed during Phases I and II of this contract. These tests consisted of subjecting in-process materials to impact, friction and ESD (electrostatic discharge) stimuli and obtaining threshold initiation levels(1) (TIL's) for each material. Results of the tests are summarized in Table I. An inspection of Table I shows that the materials in the BMR process and selected combinations are relatively insensitive. Many of the samples tested could not be initiated at the limits of the standard test machines and are so indicated when a greater than or equal sign (>) precedes a data point. For impact, the failure to initiate a sample by dropping a 2 kg weight from a height of 120 cm (over a known impact area) is the limit of the impact machine. The energy input is calibrated periodically.

(1) Level above which initiation can occur as a result of 20 consecutive failures at that level.

A friction TIL value was obtained for AN/GN/U = 45/40/15, all others exceeded the limits of the test. The maximum pressures tested at a given velocity (1 inch slide distance) are in Table I.

The TIL values for ESD ranged from 0.075 to 1.26 joules, a spread of only two test levels, and are considered to be high. They are above the energy region that could be available from a human being (0.013 joules max).

In all sensitivity testing, the Model 300 Lira Analyzer was used to determine if initiation occurred. The Lira is a precision instrument that analyzes selected components of a gas mixture to determine their presence and concentration. The Lira analyzes a sample gas by comparing its infrared absorption characteristics with the constant infrared absorption characteristics of a known gas. The Model 300 is modified to operate as a detector of the decomposition gases CO, CO_2, NO_2 and NO. Therefore, initiation does not necessarily mean that a flash fire or smoke (visual indication) will result, but rather that some decomposition occurs which produces gaseous products detected by the Lira. This is a much more critical definition of initiation.

Results of the Differential Scanning Calorimeter tests are shown in Table II. Relatively high temperatures (266 to 295°C) had to be reached before any exothermic reaction occurred.

All samples (except the pure ingredients) subjected to the various initiation sources were stoichiometric mixtures (balanced to CO_2, H_2O, N_2) that represent the "worst case" conditions that could occur in the process.

Transition Testing

Transition tests were performed to determine the effect of initiation on the ability of a material to transit from flame initiation to an explosive reaction in terms of material height under specific environmental conditions.

Critical height (transition) test results are shown in Table III. Tests on the reactor mixture were performed at both ABL and Kenvil. Initial tests were run in containers smaller than pilot plant reactor tubes with the intent of extrapolating data to determine if the reactors would transit to an explosion if the material was initiated. However, no reaction occurred in a 1" x 48" container. Therefore, a 2" x 12' test was performed at the Kenvil Plant in which no explosive reaction occurred. Since material height required for explosion to occur increases as the diameter increases, it was concluded from the Kenvil tests that an explosive reaction would not occur in the 4" x 12' pilot plant reactors if initiation occurred.

Transition tests were also performed on guanidine nitrate and no explosive reaction occur in a 1" x 24" container. Again after considering pilot plant eq it dimensions, it was concluded that no transition hazard exist pilot plant equipment handling guanidine nitrate.

Propagation Tests

Propagation tests det ine the explosive propagation characteristics of a material in terms of erial diameter when subjected to a shock stimuli. Results of thes sts are shown in Table III. The results show that guanidine nitrate an e material in the reactors will propagate an explosive reaction, sinc h of their critical diameters are less than one inch. However, it m e remembered that the transition tests demonstrated that these mater under the pilot plant conditions, would not transit to an explosion. n other words, the pilot plant process materials are not capable of supplying a shock stimulus for propagation to occur.

Propagation tests performed on other samples show that no propagation will occur in the one inch piping used in the pilot plant.

Dust Explosibility

Dust explosibility tests were performed in an effort to determine the minimum concentration and minimum energy required to initiate guanidine nitrate in a dusty atmosphere. The guanidine nitrate was screened to < 53 micron and two different sources of initiation were used. Initially a continuous sparking electrode was attempted, however, no initiation of a GN/air dust cloud could be obtained. The test was rerun using fibrous nitrocellulose as an ignition source which is a more violent source of initiation than the sparking electrodes. In both cases, the guanidine nitrate dust/air mixture could not be initiated at the standard test limits of the machine (4.1 oz/ft^3).

A possible explanation of this unexpected result can be obtained by an interpretation of the DSC data and applying it to a dust cloud ignition sequence. In order for a dust cloud to ignite and sustain ignition, dust particle(s) must be raised to their ignition temperature and the heat released by their ignition must be sufficient to ignite adjacent particles and thus result in a sustained reaction. From the DSC trace, GN melts in the range of 210 to 220°C while absorbing 30-35 cal/gm. An exotherm occurs in the range of 285-316°C liberating 90-120 cal/gm. (By comparison, RDX and nitroglycerin burn and liberate about 1200-1500 cal/gm at first exotherm). The amount of heat released is enough to raise the temperature an additional 100°C or to approximately 385 to 485°C. GN dust cloud ignition temperature ranges from 390°C (ABL data) to 500°C.(7) Therefore, it could be reasoned the ignition of GN dust particles does not result in the liberation of enough heat to ignite adjacent dust particles to sustain ignition in the dust cloud.

Based on the inability to ignite or sustain ignition of a GN dust cloud up to the concentration limits of test apparatus (4.1 oz/ft^3), it was concluded that no dust explosion hazard existed.

Shipping and Storage Classification Testing

Testing in accordance with TB-700-2 was conducted on guanidine nitrate by ABL. The data from these tests are shown on Table IV. The government has used a combination of these data and its own in-house data to tentatively classify guanidine nitrate (less than 25% water wet) as Class 7 for storage and as an oxidizing agent for shipping.

Hazard Evaluations

The engineering analysis performed on selected equipment was performed from equipment drawings, specification and maximum operating parameters furnished by Kenvil and the Research Center. Since no on-site measurements (i.e., forces, pressures, and velocities) were made, tensile strengths or yield points of materials involved(1-3) were used to obtain safety margins. In general, the safety margins found on equipment are representative of "worst case" condition, so the analysis would be conservative from a safety point of view.

In the process where equipment handles a water slurry, the analysis was based on water-free material response data, since testing was not done with water slurries. The use of water-free material values would render conservative results, since the water would most likely act as an extinguisher for any initiation. This type of an analysis, using water-free sensitivity data, would apply to start-up or shut-down modes of operation or a process "upset condition" in which a sufficient amount of water would not be present.

Some of the items in the process were not analyzed. The densitometer and evaporator had no mechanical or moving parts. The pump in the cooling system of the crystallizer was not analyzed since it will pump water containing only a small amount of ammonium nitrate (0.1% of AN). Finally, the level controllers were not analyzed, since they had low velocity movement (~ 0.06 ft/sec).

A hazards evaluation was performed on pumps, mixers, reactors, valves, centrifuges, a crystallizer and a dryer in which in-process potentials and material response data (expressed in similar engineering terms) were compared to obtain quantitative safety margins for normal and abnormal conditions. As an example, a 3450 rpm centrifugal pump with a carbon/ceramic mechanical seal was selected to pump material to the crystallizer. The velocity of the rotating seal parts was calculated to be 16.9 ft/sec with a normal pressure of 30 psi (manufacturer's specification) and an abnormal pressure of ~ 8000 psi (yield point of carbon). Figure 1 shows a friction profile of the material being pumped (less water). By a straight line extrapolation, no positive safety margin is realized at 16.9 ft/sec. The straight line extrapolation is conservative since friction profile curves take an asymptotic form. To obtain a positive safety factor, a data point at 17 ft/sec would have to be obtained or the pump speed reduced by reducing the rpm rating. Since testing above 10 ft/sec would result in damage to the friction machine, it was recommended that a pump with a reduced rpm be used. Such a change did not adversely affect the pilot plant operation and a 1750 rpm centrifugal pump with a teflon pack gland was selected. The in-process potential for the pump was 24 psi (normal) to $\sim$ 5,000 psi (abnormal) at a velocity of 8.6 ft/sec. By referring to Figure 1, material response at 8.6 ft/sec is $\sim$ 43,000 psi. By comparing the in-process potential to the material response data safety margins of 8.6 to 1797 are realized.

A similar analysis has been completed on designated pilot plant equipment. A detailed discussion with summary tables of all engineering analysis has been previously reported.(4-6) In general, all normal and some abnormal operations have adequate safety margins. Abnormal occurrences such as impellers or mix blades breaking and hitting metal parts would cause initiation (no safety margin), but as discussed in the risk analysis of this report, such events have probabilities 5×10^{-4} to 5×10^{-5} of occurring over the time of pilot plant operation.

Logic Model (Fault Tree)

The logic model is a concise and orderly description of various combinations of events that can lead to a predefined "undesired" event. The logic model is presented in a diagram or blueprint form and results in an engineering capability to identify and evaluate the overall effect of component failure, controls or human actions on the system.

To understand and follow the logic model, a basic knowledge of the symbols used is required. A list of the symbols used and their meaning is illustrated in Table V. The use of transfer symbols (triangles) deserves some comment since they are used in two ways: (1) for transferring a section of the model that has been previously developed under identical circumstances from another section, and (2) transfer similar logic from one piece of equipment that applied to another piece of equipment. Use of transfers in this second method means that only the logic or events are the same, but probabilities of the events may be different since it is a different piece of equipment handling different materials.

The uses of transfer symbols may be best explained by using an example for each of the ways they are employed. On page A-4 of the logic model, an event for possible friction initiation "Impeller hits tank wall" is developed. Under this event a transfer symbol △2C is shown. On the same page for possible impact initiation, the same event in the same tank "Impeller hits tank wall" is shown. Since the event was already developed, it is transferred by use of the symbol △2C .

On page A-8, another event "Impeller hits tank wall" is shown. The logic to develop this event is the same as that on page A-4, but applies to a different mixer. Therefore, a transfer ▽2C is used to show such a transfer. Table VI lists all transfer used and their origination point in the logic model.

Risk Analysis for Guanidine Nitrate Pilot Plant

The logic model constructed in support of this analysis yielded a total of 152 potential failure modes. Of these, only 21 of the modes were considered to be significant or critical. These failure modes would result in, at most, initiation and not transition to explosion.

These failure modes and their respective probabilities of occurrence are given in Table VII. The basic failure modes are impeller, shaft, and/or alignment. As noted, the probabilities of failure are not the same throughout Table VII. These differences arise from a careful engineering analysis of the potential failure modes and the utilization of known failure rates. Also, the probability is calculated such that 800 hours of continuous operation have been assumed.

The probability of initiation then becomes the product of the probability of failure, times the proportion of operating time the failure rate applies, times the material response probability. For example, the impeller, shaft and shaft packing for the Goulds Pump (mixing system) had a combined failure rate of seven per million operating hours ($7 \cdot 10^{-6}$). Thus, after 800 hours, the probability of failure becomes $7 \cdot 10^{-6}$ times 800 or $5.6 \cdot 10^{-4}$ as given in Table VII. Multiplying this probability of $5.6 \cdot 10^{-4}$ times the proportion of operating time it applies, times material response probability gives an overall probability of initiation, or $5.6 \cdot 10^{-4}$ times 1.0 times 0.98 or $5.6 \cdot 10^{-4}$ as given in the last column of Table VII. The other probabilities of Table VII were derived in a like manner. Thus, Table VII gives the probability of initiation for each failure mode plus the overall probability for the pilot plant, which is 4.6×10^{-3}. It must be emphasized that this probability assumed 800 hours at continuous operation without repairs or maintenance. Any such action within the 800 hours would tend to reduce this probability to a much smaller quantity.

It has been shown that no transition is possible for guanidine nitrate material. Thus, the maximum expected losses to be experienced are those related to a localized initiation.

The question immediately arises, are there cost advantages to having a preventative maintenance program to reduce the potential of initiation? The answer to the posed question lies in a trade-off study between the cost of such a program versus the expected loss should initiation occur.

Expected Loss

As indicated, if initiation occurs, it remains local as no transition to an explosion is possible. Thus, the expected loss becomes the product of the probability of initiation times the sum of the following cost:

(1) Pump or equipment replacement cost.

(2) Labor necessary to replace the pump, and clean-up from the deluge system.

(3) Production losses while the equipment is being replaced.

For the pilot plant, a liberal estimate of total cost to be incurred, if initiation arises, is $5,000. This times the probability of initiation anywhere in the pilot plant gives an expected loss of $5 \cdot 10^3 \times 4.6 \cdot 10^{-3}$ or approximately $25. It must be pointed out however, that if initiation were to occur, then the minimum loss ($5,000) would be experienced. The "expected loss concept" is a well recognized means at normalizing cost data in a risk analysis study.

With the minimal expected loss of $25, any preventative maintenance cost would far exceed the estimated loss. Thus, the answer to the question, is there a cost advantage to a preventative maintenance program is obviously, no. Therefore, over the operating interval of 800 hours, no preventative maintenance program is recommended or warranted. Again, this conclusion arises, primarily, from the lack of potential for transition.

E J Krupko
E. J. Krupko

M. L. Jones
M. L. Jones

EJK:MLJ:mjs
Attach.

TABLE I

SUMMARY OF SENSITIVITY DATA (BMR PROCESS)

		Threshold Initiation Level**			
Sample (% by wt.)	Temperature	Impact (ft-lbs/in^2)	Friction (psi/ft/sec)	ESD (Joules)	Materials
AN/U 1/1	Ambient	--	$\geq$ 69,000/8		Steel/Steel
AN/U 2/1	Ambient	--	$\geq$ 69,000/8		Steel/Steel
AN/U 4/1	Ambient	$\geq$ 59.7	$\geq$ 67,000/8	0.5	Steel/Steel
AN/U 4/1	135°C	84 x 10^3*	$\geq$ 39,090/8		Steel/Steel
AN/GN/U 45/40/15	60°C	> 77.6	45,614/8 35,185/10		Steel/Steel Steel/Steel
AN/GN/U 67/24/9	130°C		$\geq$ 58,870/10		Steel/Steel
GN - Pure	Ambient	$\geq$ 59.7	$\geq$122,400/8	1.26	Steel/Steel
GN - Technical Grade	Ambient	31.6	>105,800/8	0.075	Steel/Steel

---

* ft-lbs/sec

** Level above which initiation can occur as a result of 20 consecutive failures at that level.

TABLE II

DIFFERENTIAL SCANNING CALORIMETER (DSC) TEST RESULTS

AN/U
1/1

Heating Rate (°C/min)	
20	Endotherm at 240°C
40	--
80	--

AN/U/Sil Gel
2/2/1.7

Heating Rate (°C/min)	Exotherm Began	Peak Value
20	266°C	280°C
40	276°C	290°C
80	295°C	320°C

GN

Heating Rate (°C/min)	Exotherm Began	Peak Value
5	--	--
10	285°C	307°C
20	292°C	316°C

TABLE III

EXPLOSIVE CHARACTERISTICS OF MATERIALS

Sample	Dust Explosibility	Critical Height	Critical Diameter
GN	≥ 4.1 oz/ft^3	≥ 24" for a 1" diameter pipe	< 1" 1" dia - 2980 m/sec 2½" dia - 3980 m/sec
Reactor Mixture (200°C)		≥ 48" for a 1"(1) diameter pipe	< 1"
Reactor Mixture (200°C)		≥ 12' for a 2"(2) diameter pipe	
34/38/28 GN/AN/U at 60°C			> 1"
AN/U 4/1 at 100°C			> 1"

Propagation Test for GN in a Tray (6" deep x 12" wide x 24" long)

1" Booster - no propagation
2" Booster - propagation - 2900 m/sec

(1) Performed at ABL
(2) Performed at Kenvil Plant

TABLE IV

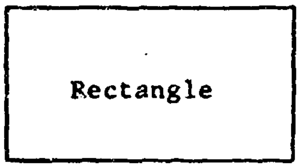
HAZARD CLASSIFICATION TESTS FOR GUANIDINE NITRATE BY TB 700-2 CRITERIA

Test	Result
Detonation Test (No. 8 Blasting Cap)	No deformation of pressure plate or cylinder
Ignition and Unconfined Burning Test	Burning reaction only
Thermal Stability Test	No color or visible change in 48 hours at 75°C
Card Gap Test	Failure at zero cards
Impact Sensitivity Test	No ignition at 47.3 inches (120 cm)

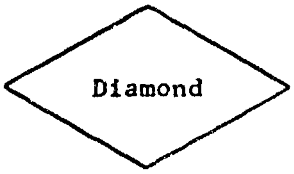
TABLE V

GLOSSARY OF SYMBOLS COMMONLY EMPLOYED ON FAULT TREE DRAWINGS

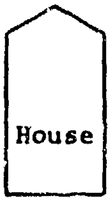
Event Representation



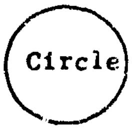
The rectangle identifies an event that results from the combination of fault or hazard events through the input logic gate.



The diamond describes a fault or hazard that is basic in a given fault tree, but undeveloped at this level. The reasons for it being undeveloped are, necessary information not available, insufficient consequence or limited scope of analysis.



The house indicates an event that is normally expected to occur.



The circle describes a basic fault event that requires no further development.

Logic Operations

"And Gate" describes the logical operation whereby the coexistence of all input events is required to produce the output event.

TABLE V (CONTINUED)

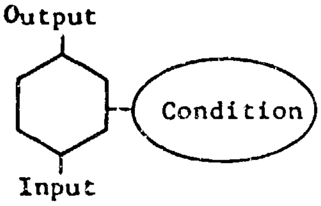
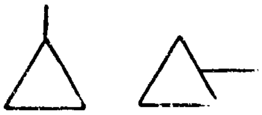
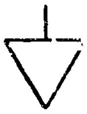
	"Or Gate" defines the situation whereby the output event will exist if one or more of the input events exist.
Inhibit Gate 	Inhibit gates describe a casual relationship between one fault and another. The input event directly produces the output event if the indicated condition is satisfied.
Triangles 	The triangles are used as transfer symbols. A line from the apex of the triangle indicates a "transfer in" and a line from the side denotes a "transfer out."
	Similarity transfer. It denotes the transfer of <u>logic</u> <u>only</u> from another part of the tree.

TABLE VI

ORIGINATION POINT FOR TRANSFER SYMBOLS IN THE LOGIC MODEL

Transfer	Origination (page)
1A	A-2
1B	A-2
1C	A-2
1D	A-2
2A	A-4
2B	A-4
2C	A-4
2D	A-5
2F	A-5
2G	A-5
2H	A-3
2J	A-3
2K	A-3
2L	A-3
2M	A-3
3A	A-6
3B	A-7
3C	A-7
3D	A-6
3E	A-6
3F	A-7
3H	A-7
3J	A-7
3K	A-7
4A	A-9
4B	A-8
4C	A-10
4D	A-10
4E	A-10
4F	A-10
4G	A-9
5A	A-11
5C	A-11
5D	A-11
5E	A-11
5F	A-12
6A	A-13
6B	A-14
6C	A-15
6D	A-15
6E	A-13
6F	A-15
7A	A-16
7B	A-16
7C	A-17
7D	A-17
7E	A-18
7F	A-18
7G	A-17
7H	A-18
8A	A-20
8B	A-20
8C	A-20
8D	A-20
9A	A-19
9B	A-19
9C	A-19

TABLE VII. PROBABILITIES OF FAILURE SUMMARY FOR CRITICAL FAILURE MODES

Item	Failure	Type of Hazard	Failure Probability(1)	Proportion of Time Failure Applies(2)	Material Response Probability	Probability of Initiation
Mixer (Mixing System)	Impeller, Shaft	Impact Friction	5.6×10^{-5} 5.6×10^{-5}	1.0 1.0	0.98 0.98	5.5×10^{-5} 5.5×10^{-5}
Goulds Pump (Mixing System)	Impeller, Shaft, or Shaft Packing	Impact Friction	5.6×10^{-4} 5.6×10^{-4}	1.0 1.0	0.98 0.98	5.5×10^{-4} 5.5×10^{-4}
Goulds Pump (Reaction System)	Impeller, Shaft or Shaft Packing	Impact Friction	5.6×10^{-4} 5.6×10^{-4}	1.0 1.0	0.98 0.98	5.5×10^{-4} 5.5×10^{-4}
Mixer (Aqueous Quench)	Impeller or Shaft	Impact Friction	5.6×10^{-5} 5.6×10^{-5}	1.0 1.0	0.98 0.98	5.5×10^{-5} 5.5×10^{-5}
Goulds Pump (Aqueous Quench)	Impeller, Shaft or Shaft Packing	Impact Friction	5.6×10^{-4} 5.6×10^{-4}	1.0 1.0	0.98 0.98	5.5×10^{-4} 5.5×10^{-4}
Mixer (Crystallizer System)	Impeller or Shaft	Impact Friction	5.6×10^{-5} 5.6×10^{-5}	0.5 0.5	0.98 0.98	2.7×10^{-5} 2.7×10^{-5}
Goulds Pump (Crystalizer System)	Impeller, Shaft or Shaft Packing	Impact Friction	5.6×10^{-4} 5.6×10^{-4}	0.5 0.5	0.98 0.98	2.7×10^{-4} 2.7×10^{-4}
Crystallizer (Crystallizer System)	Impeller, Shaft, Bearings or Improper Alignment	Impact Friction	1.9×10^{-4} 1.9×10^{-4}	0.5 0.5	0.98 0.98	9.3×10^{-5} 9.3×10^{-5}
Goulds Pump (Centrifuge System)	Impeller, Shaft or Shaft Packing	Impact Friction	5.6×10^{-4} 5.6×10^{-4}	0.125 0.125	0.98 0.98	6.8×10^{-5} 6.8×10^{-5}
Dryer	Paddle, Shaft or Shaft Bearings	Impact	1.3×10^{-4}	1.0	0.7	9.1×10^{-5}
Goulds Pump (Evaporation)	Impeller, Shaft or Shaft Packing	Impact Friction	5.6×10^{-4} 5.6×10^{-4}	0.1 0.1	0.98 0.98	5.5×10^{-5} 5.5×10^{-5}
			(System) Probability of Initiation			46.4×10^{-4}
			(System) Reliability			0.99536

(1) Failure rate times 800 hours.

(2) Proportion of hours out of 800 the equipment will be operating.

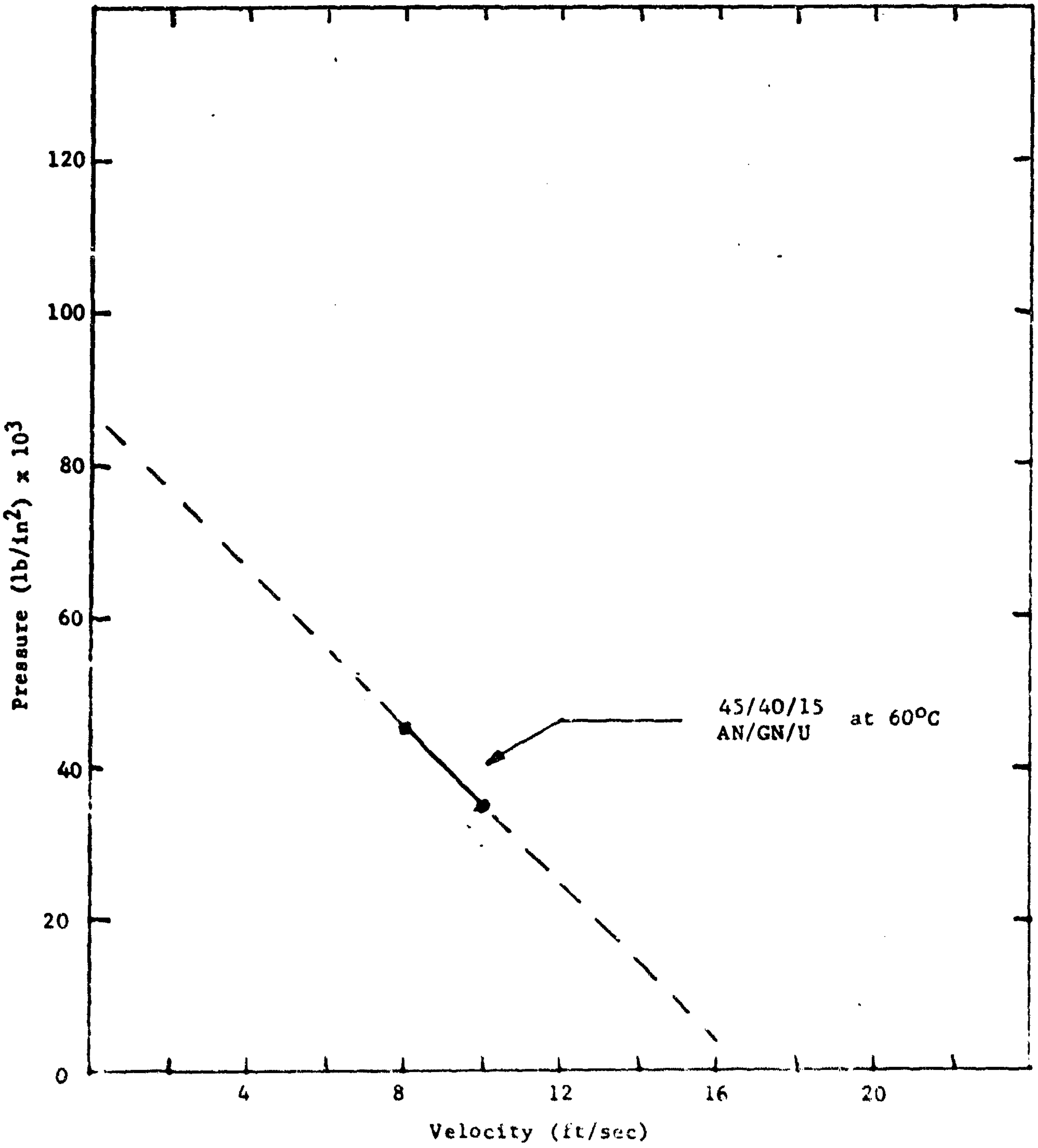
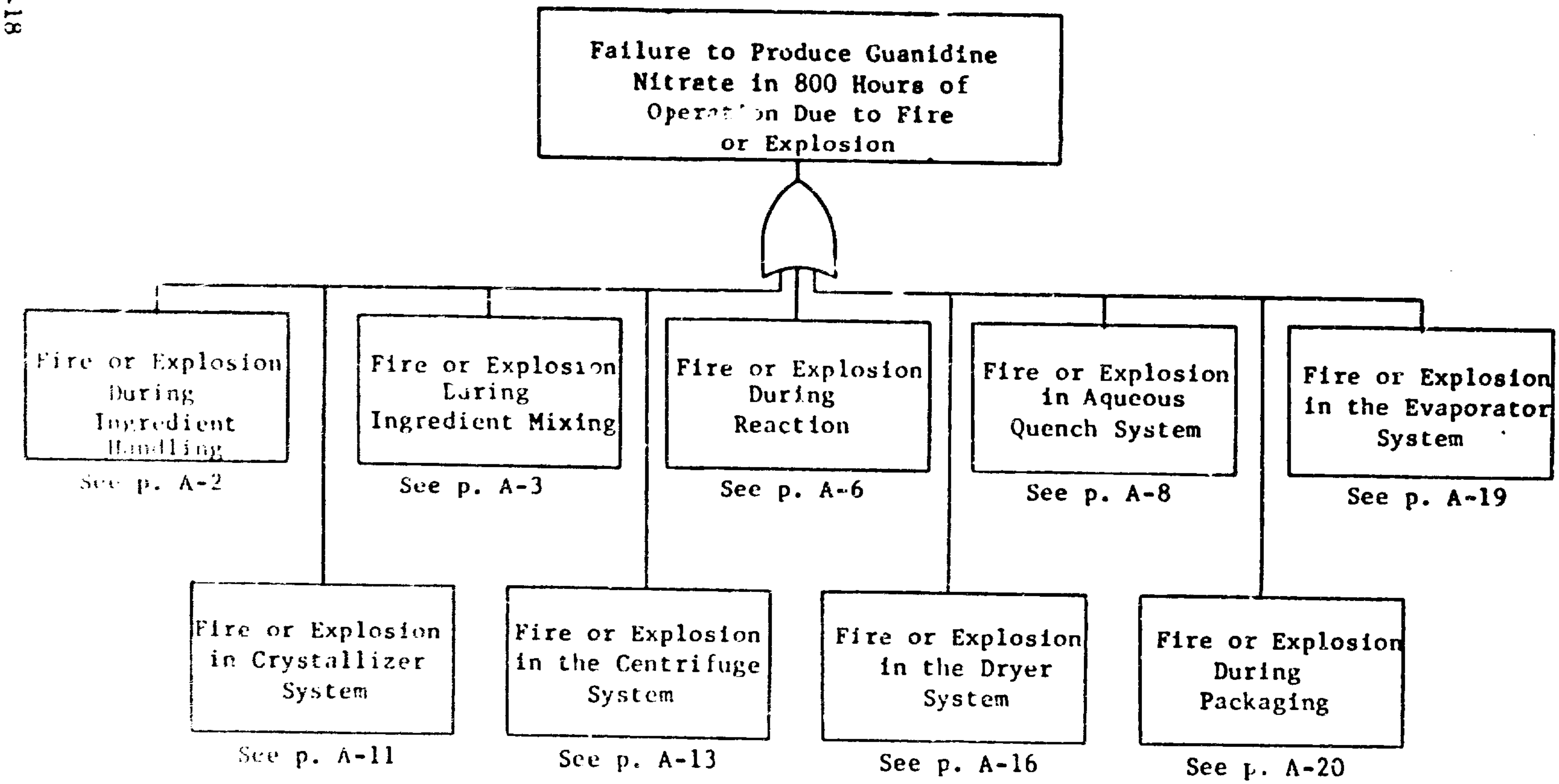
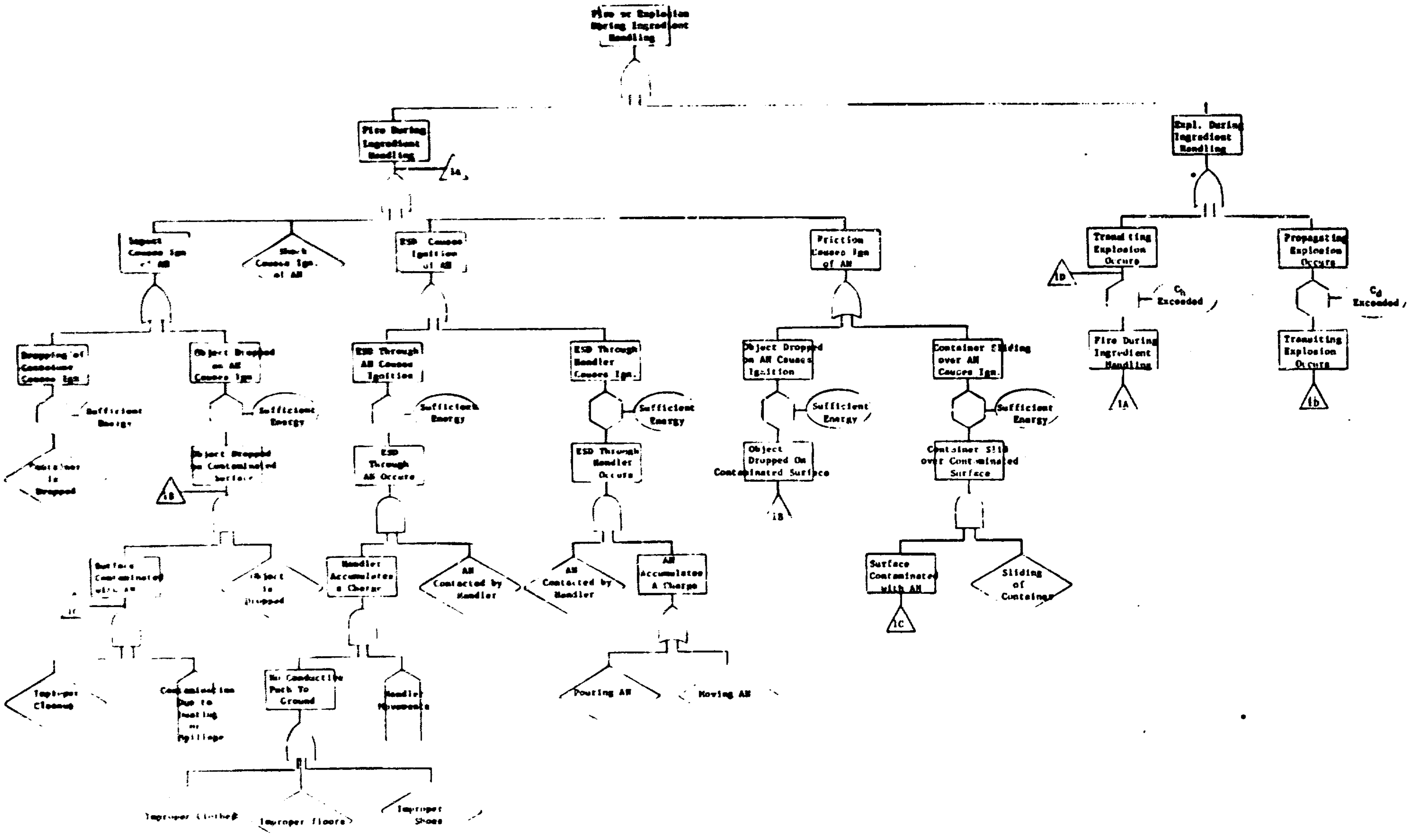
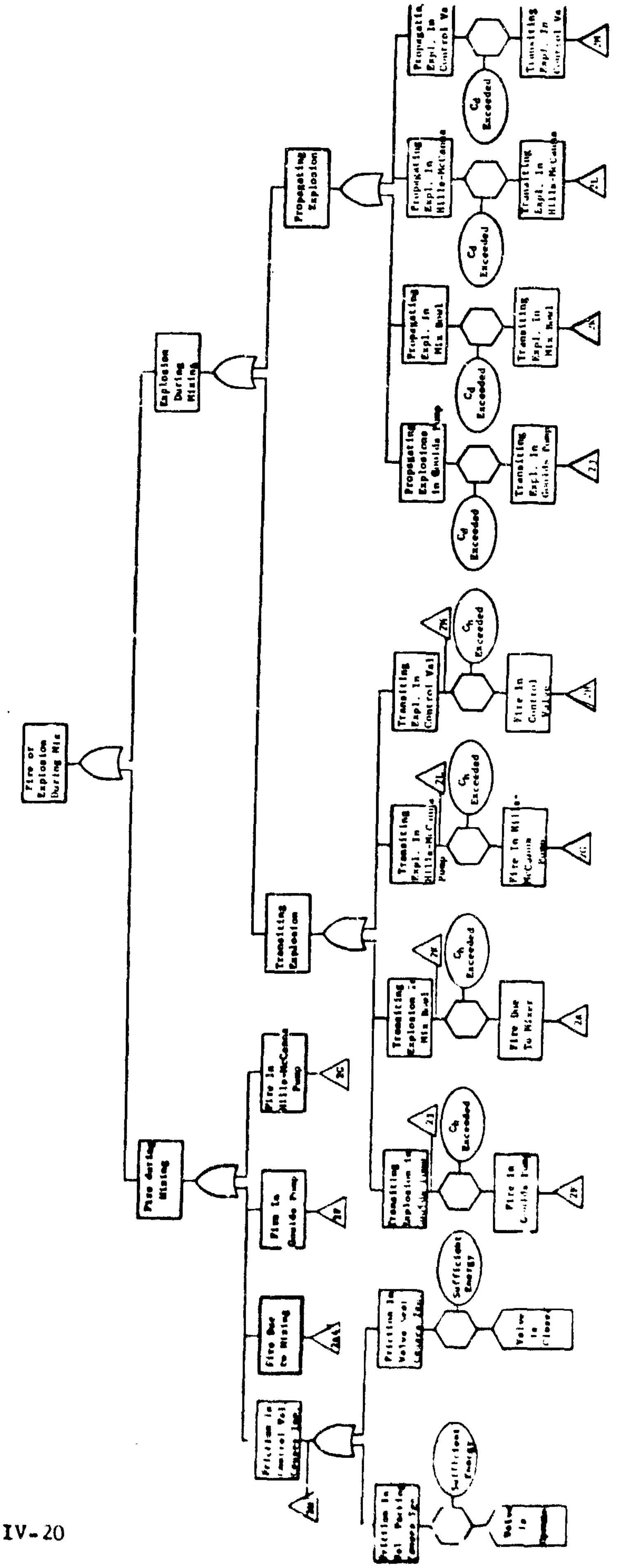
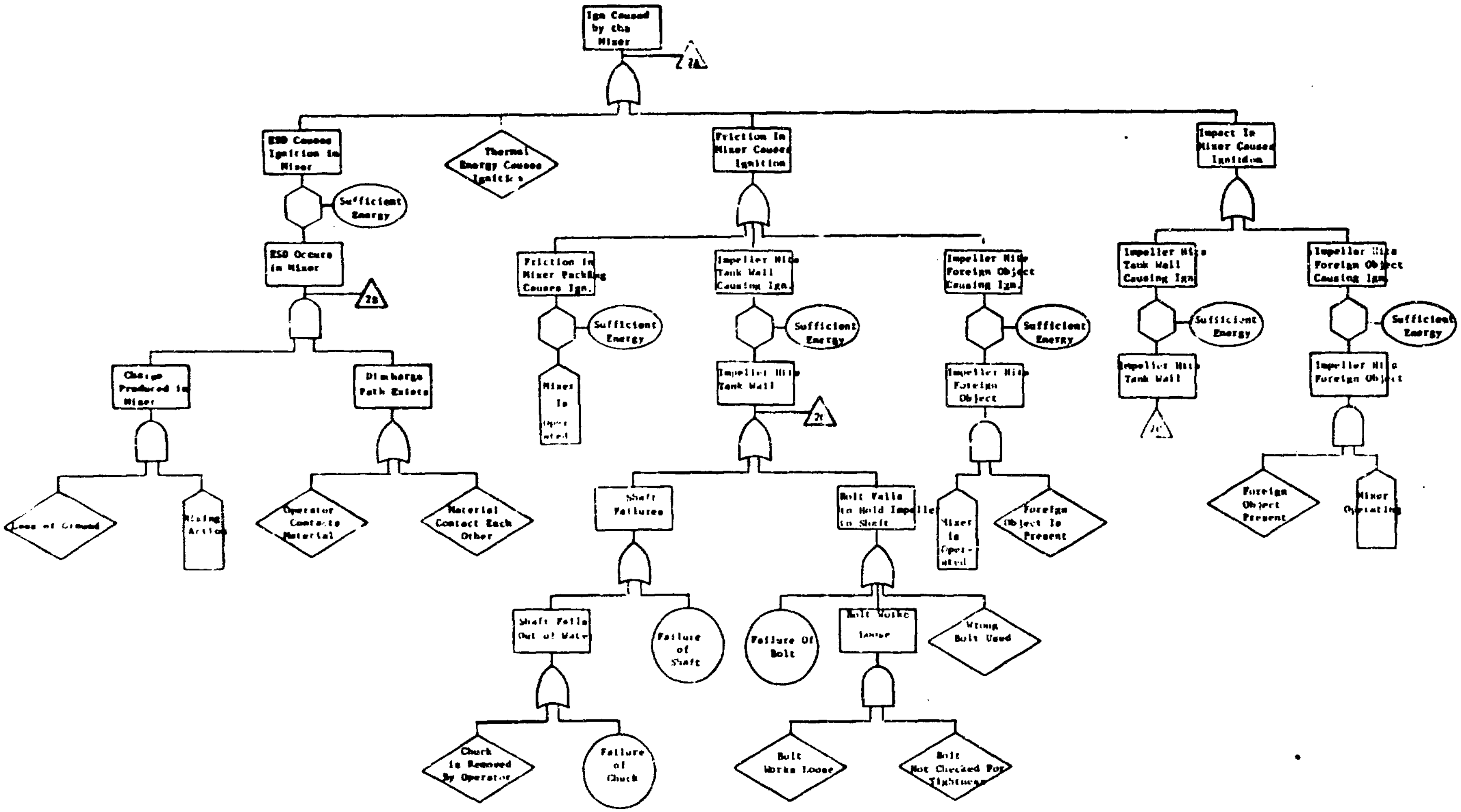


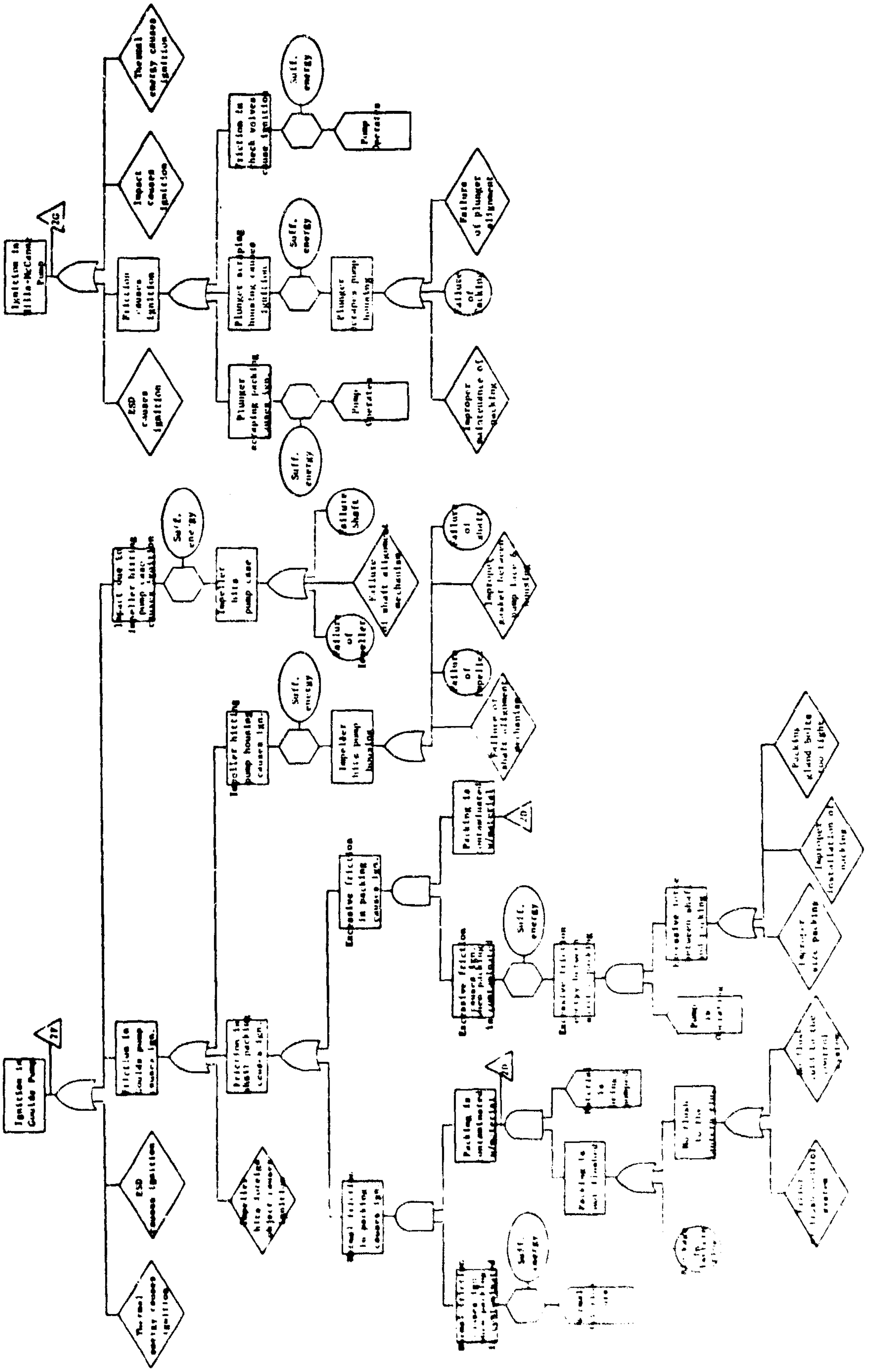
Figure 1. Friction Profile (Pressure vs. Velocity)


Failure to Produce Guanidine Nitrate in 800 Hours of Operation Due to Fire or Explosion
Fire or Explosion During Ingredient Handling
See p. A-2
Fire or Explosion During Ingredient Mixing
See p. A-3
Fire or Explosion During Reaction
See p. A-6
Fire or Explosion in Aqueous Quench System
See p. A-8
Fire or Explosion in the Evaporator System
See p. A-19
Fire or Explosion in Crystallizer System
See p. A-11
Fire or Explosion in the Centrifuge System
See p. A-13
Fire or Explosion in the Dryer System
See p. A-16
Fire or Explosion During Packaging
See p. A-20

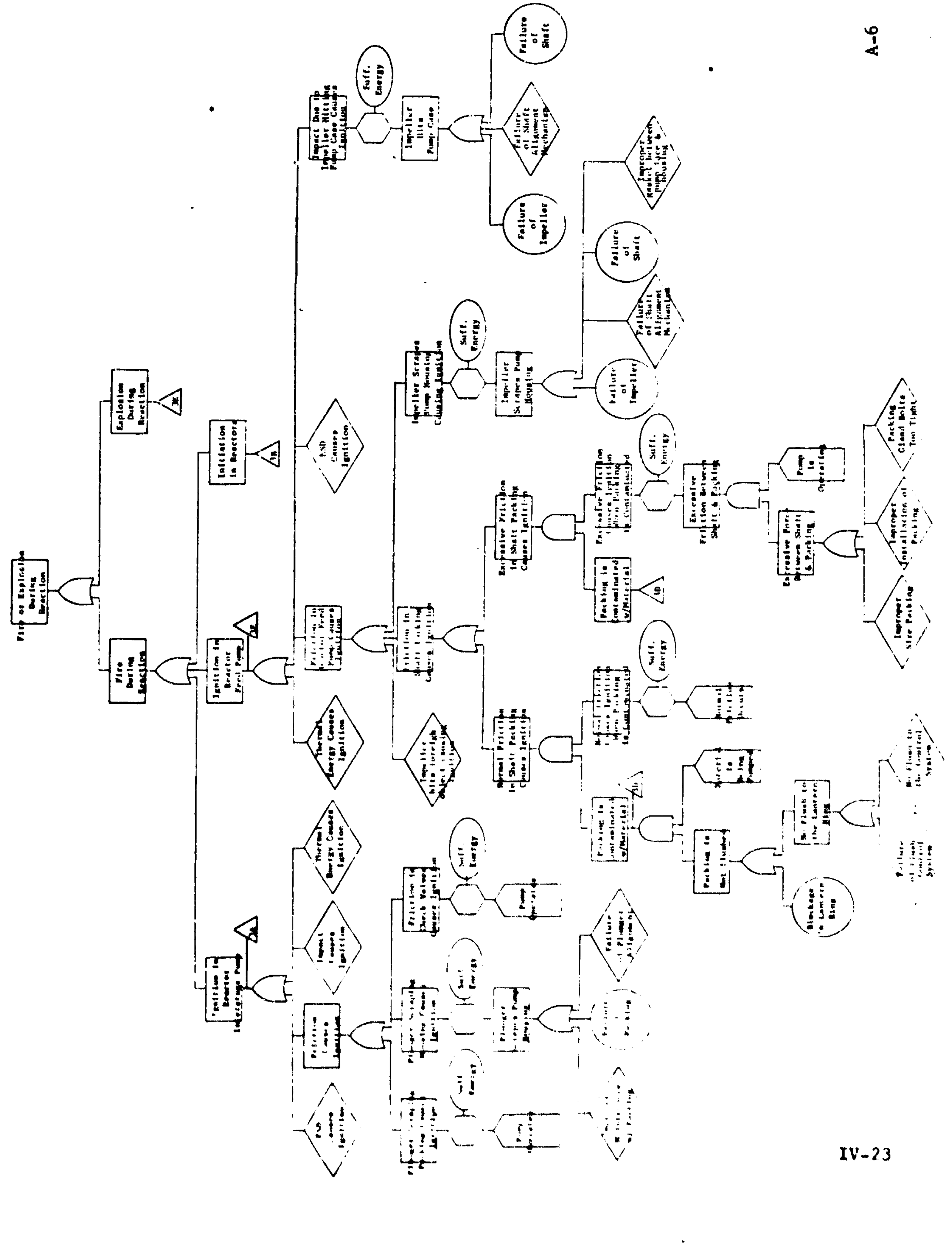

Fire or Explosion During Ingredient Handling
Fire During Ingredient Handling
1A
Expl. During Ingredient Handling
Impact Causes Ign. of AN
Shock Causes Ign. of AN
ESD Causes Ignition of AN
Friction Causes Ign of AN
Transiting Explosion Occurs
1D
Cn Exceeded
Fire During Ingredient Handling
1A
Propagating Explosion Occurs
Cd Exceeded
Transiting Explosion Occurs
1b
Dropping of Container Causes Ign
Sufficient Energy
Container is Dropped
Object Dropped on AN Causes Ign
Sufficient Energy
Object Dropped on Contaminated Surface
1B
Surface Contaminated with AN
1C
Object is Dropped
Improper Cleanup
Contamination Due to Loading or Spillage
ESD Through AN Causes Ignition
Sufficient Energy
ESD Through AN Occurs
Handler Accumulates a Charge
AN Contacted by Handler
No Conductive Path To Ground
Handler Movements
Improper Clothes
Improper floors
Improper Shoes
ESD Through Handler Causes Ign.
Sufficient Energy
ESD Through Handler Occurs
AN Contacted by Handler
AN Accumulates A Charge
Pouring AN
Moving AN
Object Dropped on AN Causes Ignition
Sufficient Energy
Object Dropped On Contaminated Surface
1B
Container Sliding over AN Causes Ign.
Sufficient Energy
Container Slid over Contaminated Surface
Surface Contaminated with AN
1C
Sliding of Container


Fire or Explosion During Mix
Explosion During Mixing
Fire during Mixing
Propagating Explosion
Transiting Explosion
Propagating Explosions In Gnulde Pump
Propagating Expl. In Mix Bowl
Propagating Expl. In Hills-McCanna
Propagating Expl. In Control Va
Transiting Expl. In Gnulde Pump
Transiting Expl. In Mix Bowl
Transiting Expl. In Hills-McCanna
Transiting Expl. In Control Va
C_d Exceeded
C_h Exceeded
Transiting Explosion In Gnulde Pump
Transiting Explosion In Mix Bowl
Transiting Expl. In Hills-McCanna Pump
Transiting Expl. In Control Val
Fire In Gnulde Pump
Fire Due To Mixer
Fire In Hills-McCanna Pump
Fire In Control Valve
Fire In Hills-McCanna Pump
Fire In Gnulde Pump
Fire Due to Mixing
Friction In Control Val
Friction In Valve Seal
Friction In Pol Positive
Sufficient Energy
Valve Is Closed
Valve Is
2A
2B
2C
2F
2G
2I
2J
2K
2L
2M
2N

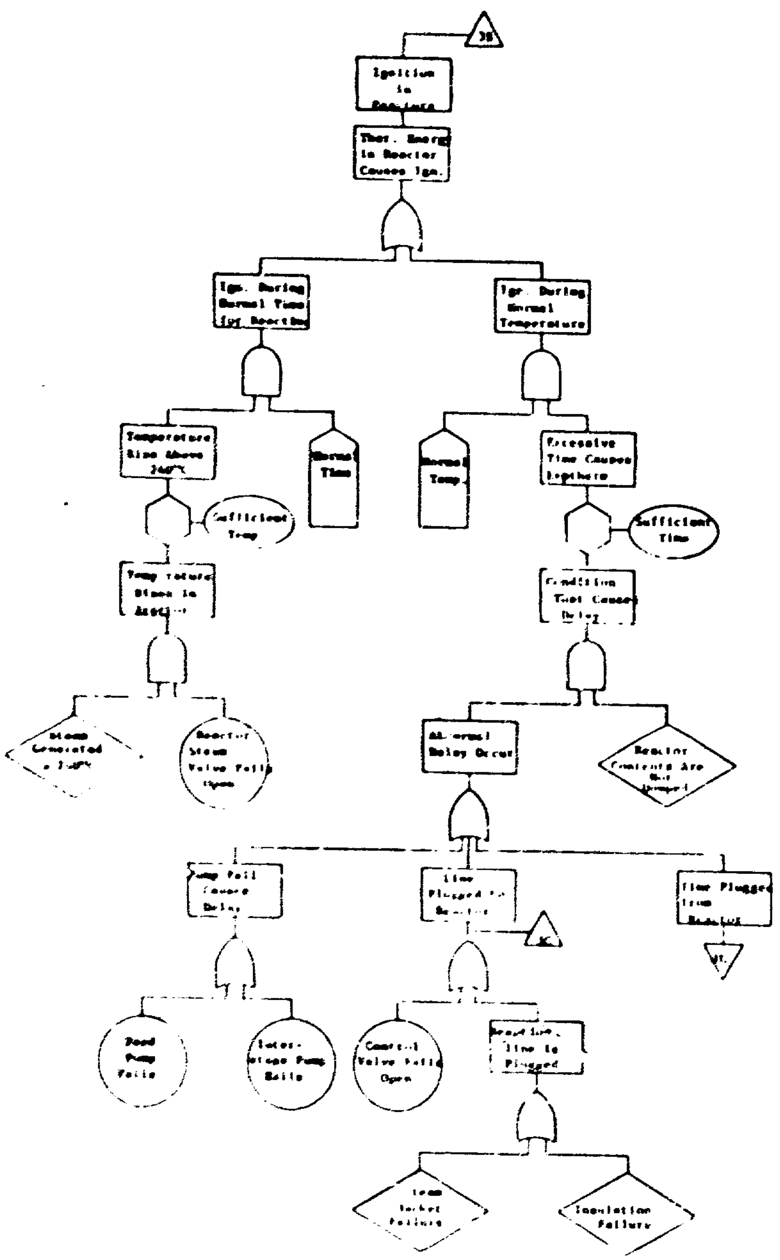

Ign Caused by the Mixer
2A
ESD Causes Ignition in Mixer
Sufficient Energy
ESD Occurs in Mixer
2B
Charge Produced in Mixer
Loss of Ground
Mixing Action
Discharge Path Exists
Operator Contacts Material
Material Contact Each Other
Thermal Energy Causes Ignition
Friction In Mixer Caused Ignition
Friction In Mixer Packing Causes Ign.
Sufficient Energy
Mixer Is Operated
Impeller Hits Tank Wall Causing Ign.
Sufficient Energy
Impeller Hits Tank Wall
2C
Shaft Failures
Shaft Falls Out of Water
Chuck Is Removed By Operator
Failure of Chuck
Failure of Shaft
Bolt Fails to Hold Impeller to Shaft
Failure Of Bolt
Bolt Works Loose
Bolt Works Loose
Bolt Not Checked For Tightness
Wrong Bolt Used
Impeller Hits Foreign Object Causing Ign.
Sufficient Energy
Impeller Hits Foreign Object
Mixer Is Operated
Foreign Object Is Present
Impact In Mixer Caused Ignition
Impeller Hits Tank Wall Causing Ign.
Sufficient Energy
Impeller Hits Tank Wall
2C
Impeller Hits Foreign Object Causing Ign.
Sufficient Energy
Impeller Hits Foreign Object
Foreign Object Present
Mixer Operating

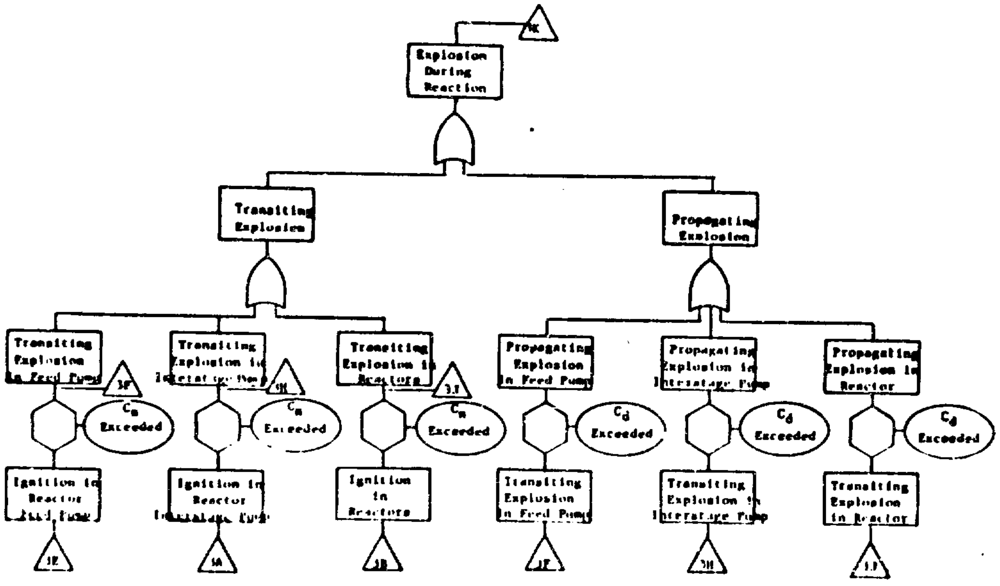

Ignition in Goulds Pump
2F
Thermal energy causes ignition
ESD causes ignition
Friction in Goulds pump causes ign.
Impact due to impeller hitting pump case causes ignition
Suff. energy
Impeller hits pump case
Failure of impeller
Failure of shaft alignment mechanism
Failure Shaft
Impeller hitting pump housing causes ign.
Suff. energy
Impeller hits pump housing
Failure of impeller
Failure of shaft alignment mechanism
Failure of shaft
Improper gasket between pump case & housing
Friction in shaft packing causes ign.
Impeller hits foreign object causes ignition
Excessive friction in packing causes ign.
Packing is contaminated w/material
2D
Suff. energy
Excessive friction energy between shaft & packing
Pump in operation
Excessive force between shaft and packing
Improper size packing
Improper installation of packing
Packing gland bolts too tight
Normal friction in packing causes ign.
Packing is contaminated w/material
2D
Packing is not flushed
No flush to the packing
Suff. energy
Ignition in Hills-McCanna Pump
2G
ESD causes ignition
Friction causes ignition
Impact causes ignition
Thermal energy causes ignition
Plunger escaping packing causes ign.
Suff. energy
Pump operates
Plunger escaping housing causes ignition
Suff. energy
Plunger strikes pump housing
Improper maintenance of packing
Failure of packing
Failure of plunger alignment
Friction in check valves cause ignition
Suff. energy
Pump operates

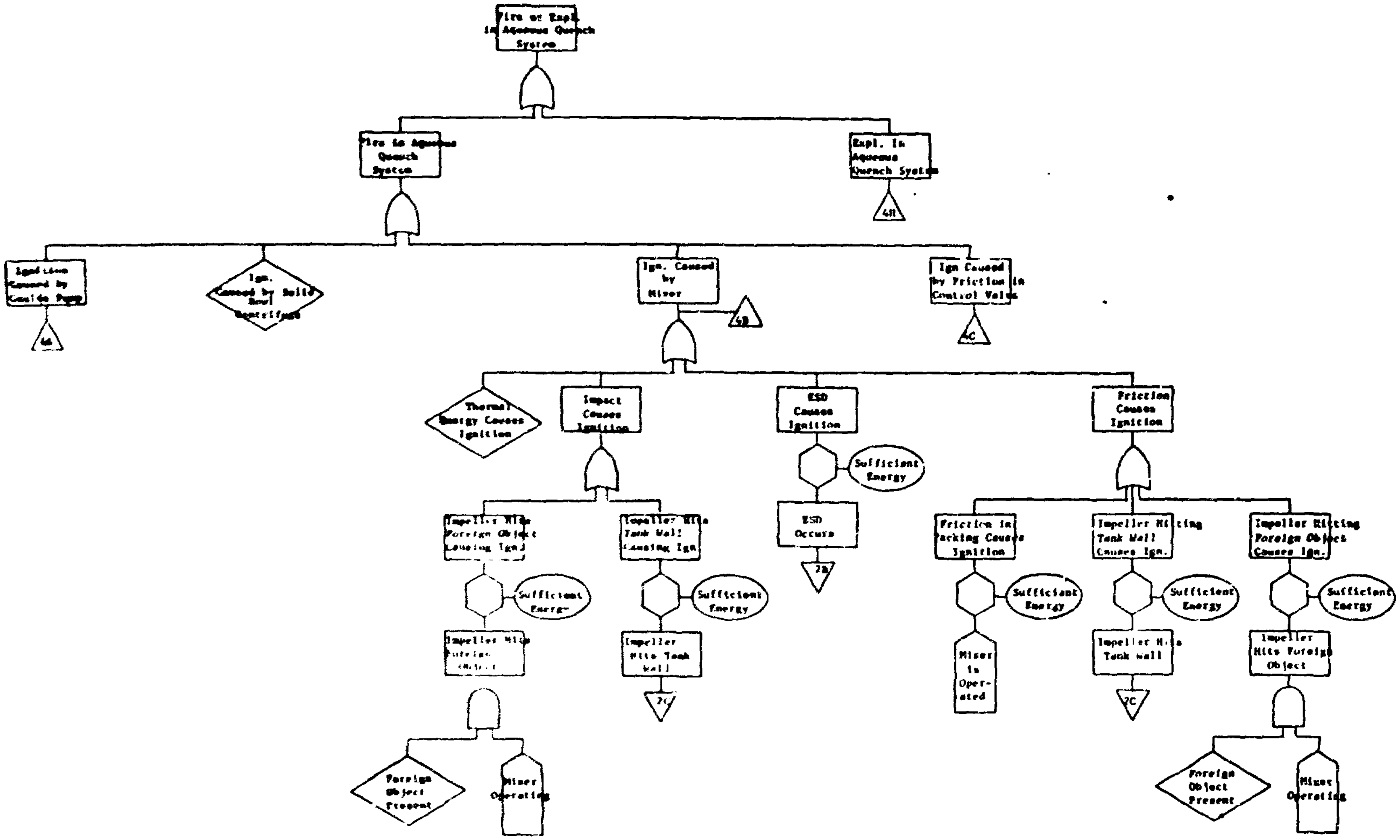
A-6

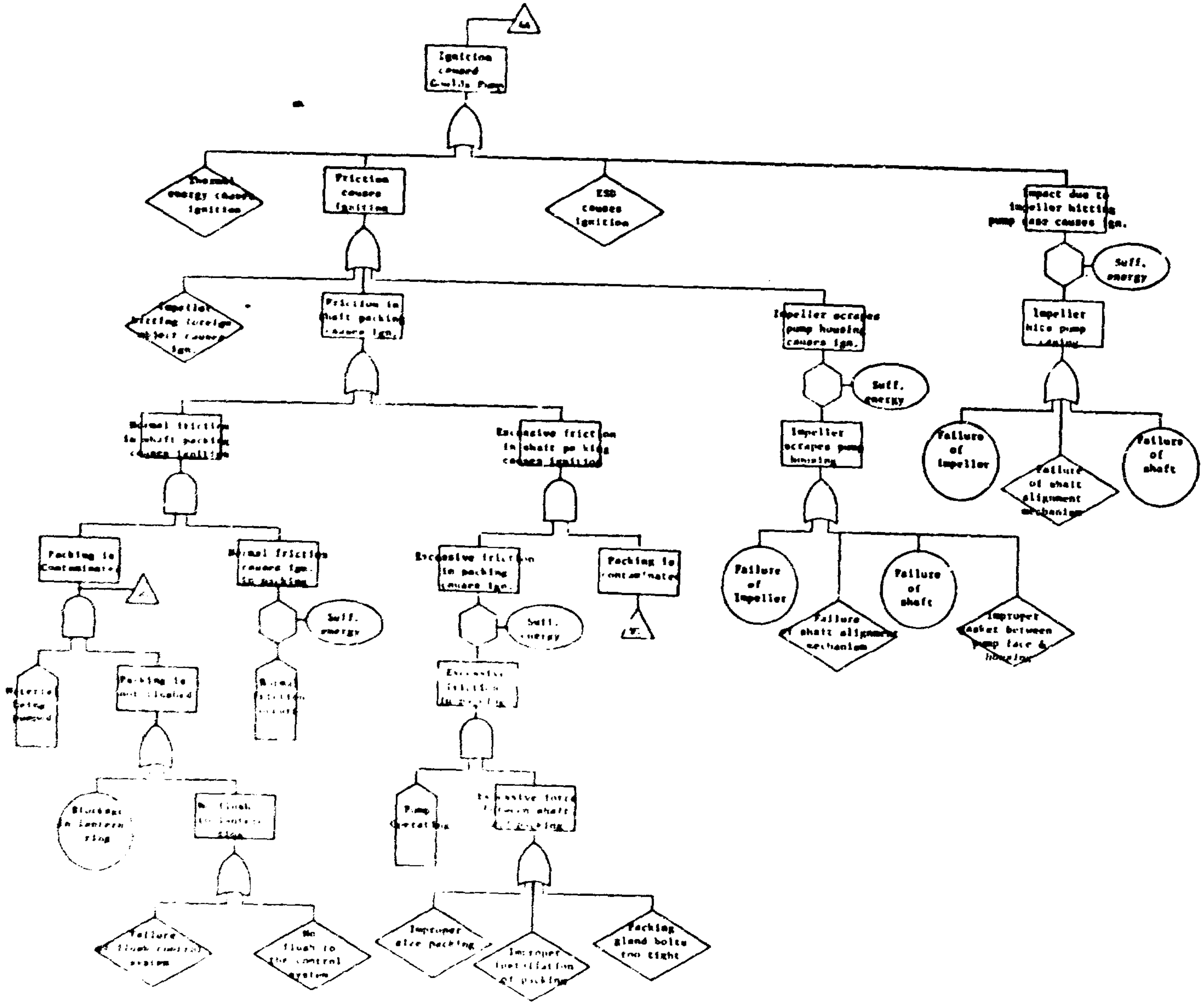


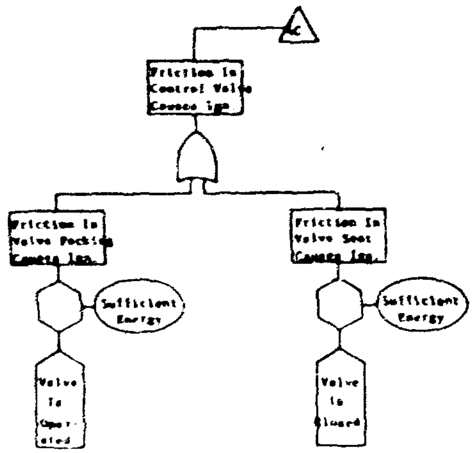
Fire or Explosion During Reaction
Explosion During Reaction
Fire During Reaction
Initiation in Reactor
Ignition in Reactor Feed Pump
Ignition in Reactor Intensifier Pump
Impact Due to Impeller Hitting Pump Case Causes Ignition
Suff. Energy
Impeller Hits Pump Case
Failure of Impeller
Failure of Shaft Alignment Mechanism
Failure of Shaft
ESD Causes Ignition
Friction in Reactor Feed Pump Causes Ignition
Thermal Energy Causes Ignition
Impeller Scrapes Pump Housing Causing Ignition
Impeller Scrapes Pump Housing
Improper Gasket between Pump Lips & Housing
Friction in Shaft Packing Causes Ignition
Impeller Hits Foreign Object Causing Ignition
Excessive Friction in Shaft Packing Causes Ignition
Packing is Contaminated w/Material
Excessive Friction Causes Ignition When Packing is Contaminated
Excessive Friction Between Shaft & Packing
Pump in Operation
Excessive Force Between Shaft & Packing
Improper Size Packing
Improper Installation of Packing
Packing Gland Bolts Too Tight
Normal Friction in Shaft Packing Causes Ignition
Normal Friction Causes Ignition When Packing is Contaminated
Normal Friction Present
Material in Being Pumped
Packing is Not Flushed
No Flush to the Lantern Ring
No Flush to the Control System
Failure of Flush Control System
Blockage in Lantern Ring
Impact Causes Ignition
Friction Causes Ignition
Friction in Check Valves Causes Ignition
Pump Operating
Plunger Scrapes Housing Causes Ignition
Plunger Scrapes Pump Housing
Failure of Plunger Alignment
Failure of Packing
Plunger Friction in Packing Causes Ignition
Pump Operating
Failure of Packing
ESD Causes Ignition

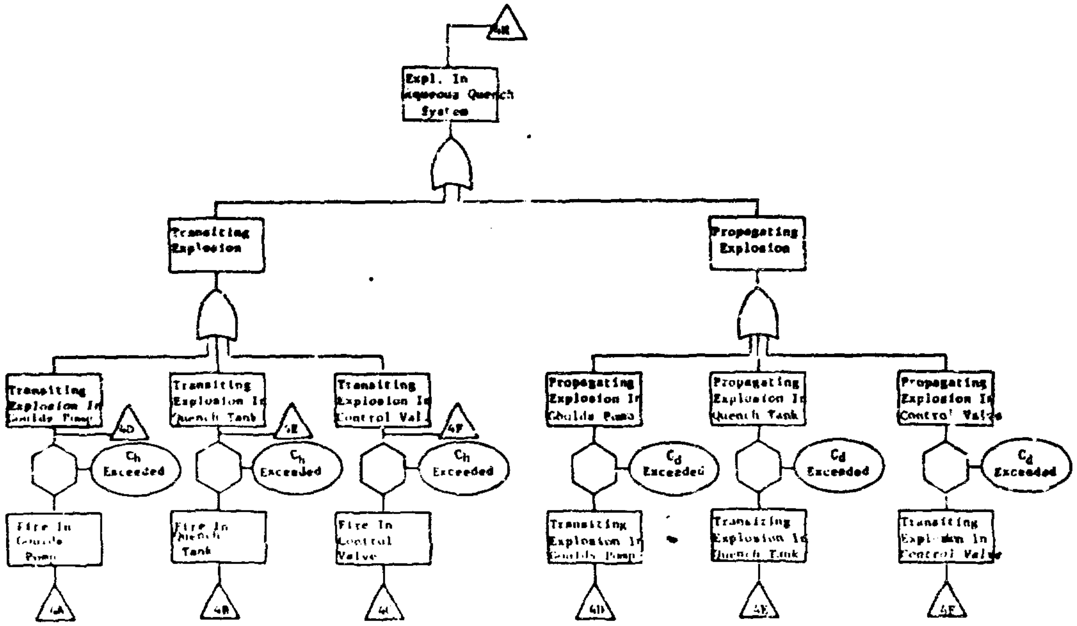

3B
Ignition in Reactors
Ther. Energy in Reactor Causes Ign.
Ign. During Normal Time for Reaction
Ign. During Normal Temperature
Temperature Rise Above 240°C
Normal Time
Normal Temp.
Excessive Time Causes Exotherm
Sufficient Temp
Sufficient Time
Temperature Rises in Reactor
Condition That Causes Delay
Steam Generated > 240°C
Reactor Steam Valve Fails Open
Abnormal Delay Occur
Reactor Contents Are Not Dumped
Pump Fail Causes Delay
Line Plugged to Reactor
Line Plugged from Reactor
3K
3L
Feed Pump Fails
Inter-stage Pump Fails
Control Valve Fails Open
Reaction Line is Plugged
Team Jacket Failure
Insulation Failure

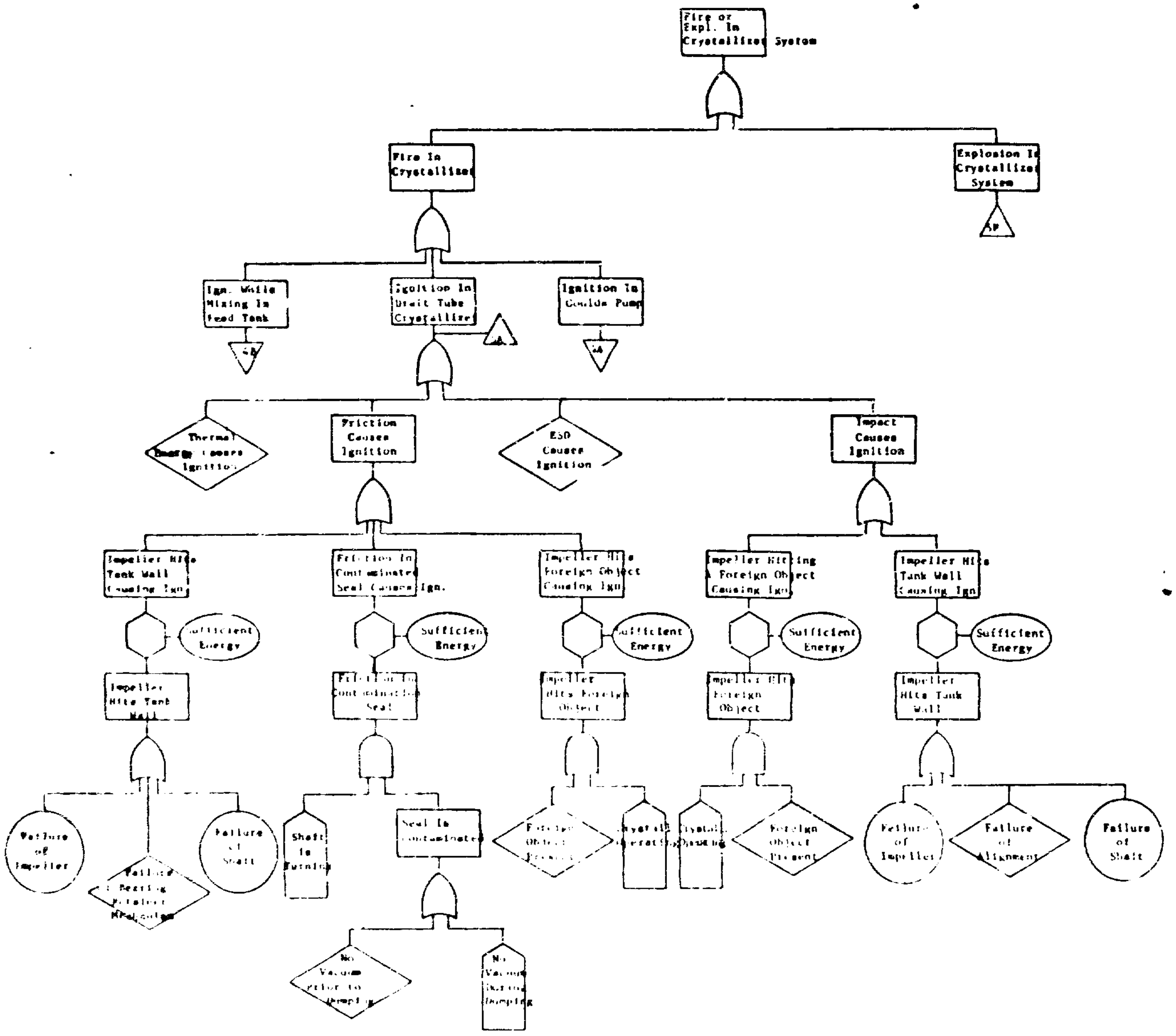

3K
Explosion During Reaction
Transiting Explosion
Propagating Explosion
Transiting Explosion in Feed Pump
Transiting Explosion in Interstage Pump
Transiting Explosion in Reactors
Propagating Explosion in Feed Pump
Propagating Explosion in Interstage Pump
Propagating Explosion in Reactor
3F
3H
3J
C_m Exceeded
C_m Exceeded
C_m Exceeded
C_d Exceeded
C_d Exceeded
C_d Exceeded
Ignition in Reactor Feed Pump
Ignition in Reactor Interstage Pump
Ignition in Reactors
Transiting Explosion in Feed Pump
Transiting Explosion in Interstage Pump
Transiting Explosion in Reactor
3E
3A
3B
3F
3H
3J

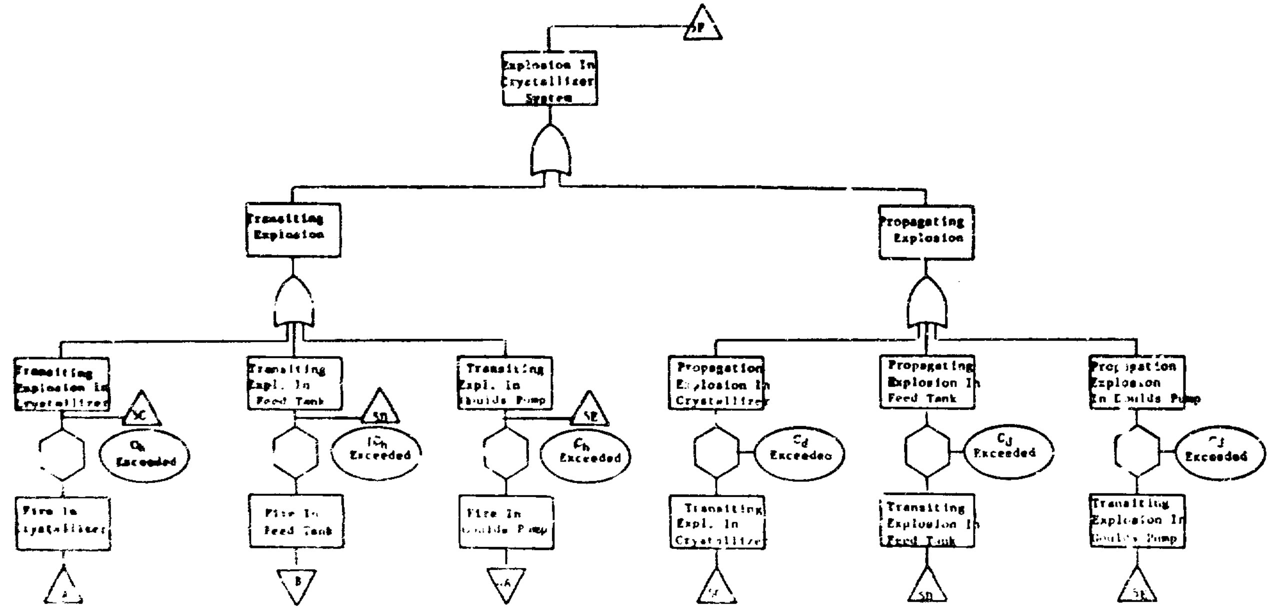

Fire or Expl. in Aqueous Quench System
Fire in Aqueous Quench System
Expl. in Aqueous Quench System
4B
Ignition Caused by Centrifuge Pump
4A
Ign. Caused by Solid Bowl Centrifuge
Ign. Caused by Mixer
4B
Ign Caused by Friction in Control Valve
4C
Thermal Energy Causes Ignition
Impact Causes Ignition
ESD Causes Ignition
Friction Causes Ignition
Impeller Hits Foreign Object Causing Ign.
Impeller Hits Tank Wall Causing Ign
Sufficient Energy
Sufficient Energy
Impeller Hits Foreign Object
Impeller Hits Tank Wall
2C
Foreign Object Present
Mixer Operating
Sufficient Energy
ESD Occurs
2B
Friction in Packing Causes Ignition
Impeller Hitting Tank Wall Causes Ign.
Impeller Hitting Foreign Object Causes Ign.
Sufficient Energy
Sufficient Energy
Sufficient Energy
Mixer is Operated
Impeller Hits Tank Wall
2C
Impeller Hits Foreign Object
Foreign Object Present
Mixer Operating

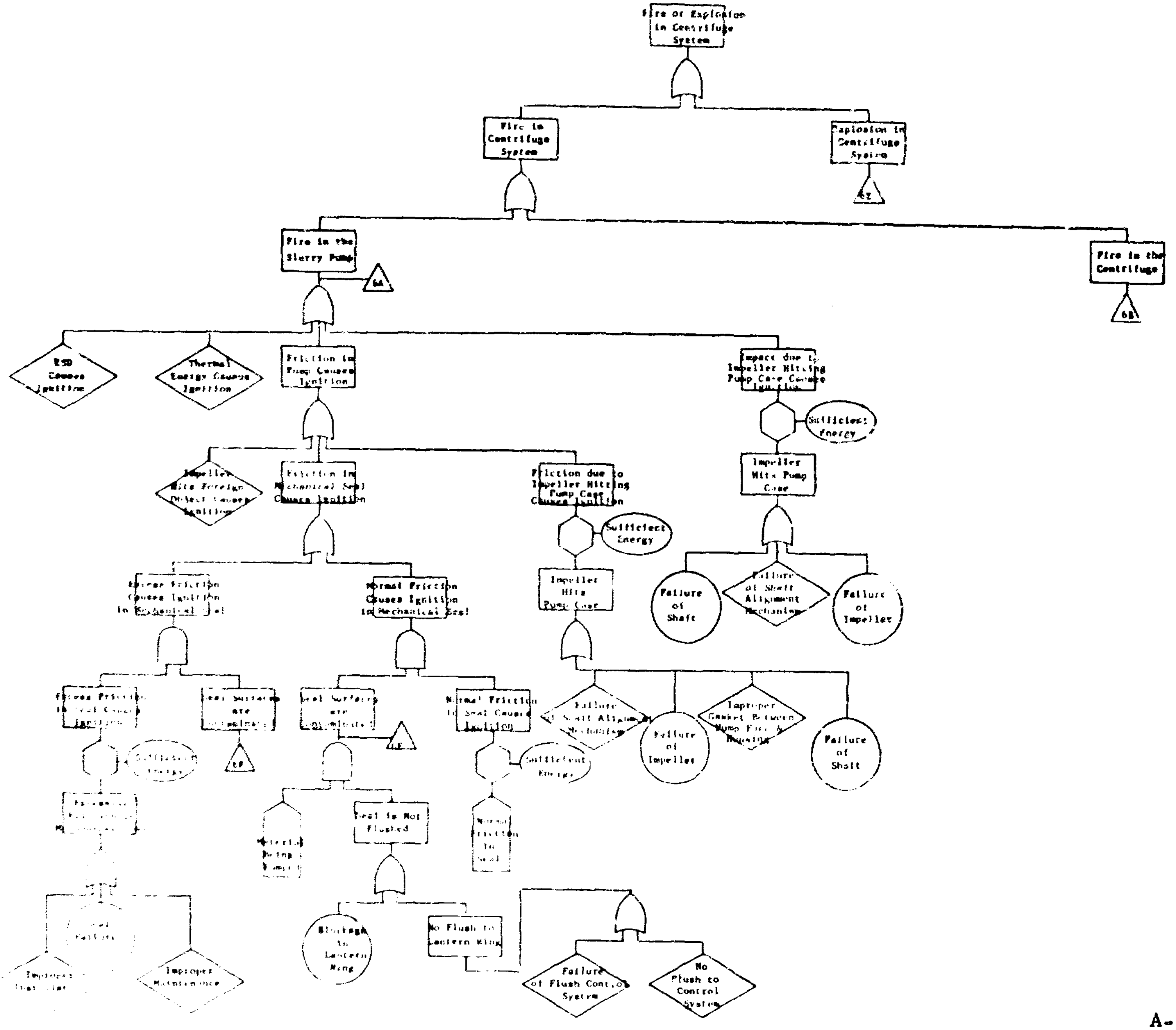

6A
Ignition caused C-well's Pump
Thermal energy causes ignition
Friction causes ignition
ESD causes ignition
Impact due to impeller hitting pump case causes ign.
Suff. energy
Impeller hits pump casing
Failure of Impeller
Failure of shaft alignment mechanism
Failure of shaft
Impeller hitting foreign object causes ign.
Friction in shaft packing causes ign.
Impeller scrapes pump housing causes ign.
Suff. energy
Impeller scrapes pump housing
Failure of Impeller
Failure of shaft alignment mechanism
Failure of shaft
Improper gasket between pump face & housing
Normal friction in shaft packing causes ignition
Excessive friction in shaft packing causes ignition
Packing is Contaminated
Material being pumped
Packing is not flushed
Blockage in lantern ring
No flush to lantern ring
Failure of flush control system
No flush to the control system
Normal friction causes ign. in packing
Suff. energy
Normal friction occurs
Excessive friction in packing causes ign.
Suff. energy
Excessive friction in packing
Pump Operating
Excessive force between shaft & packing
Improper size packing
Improper installation of packing
Packing gland bolts too tight
Packing is contaminated
V.

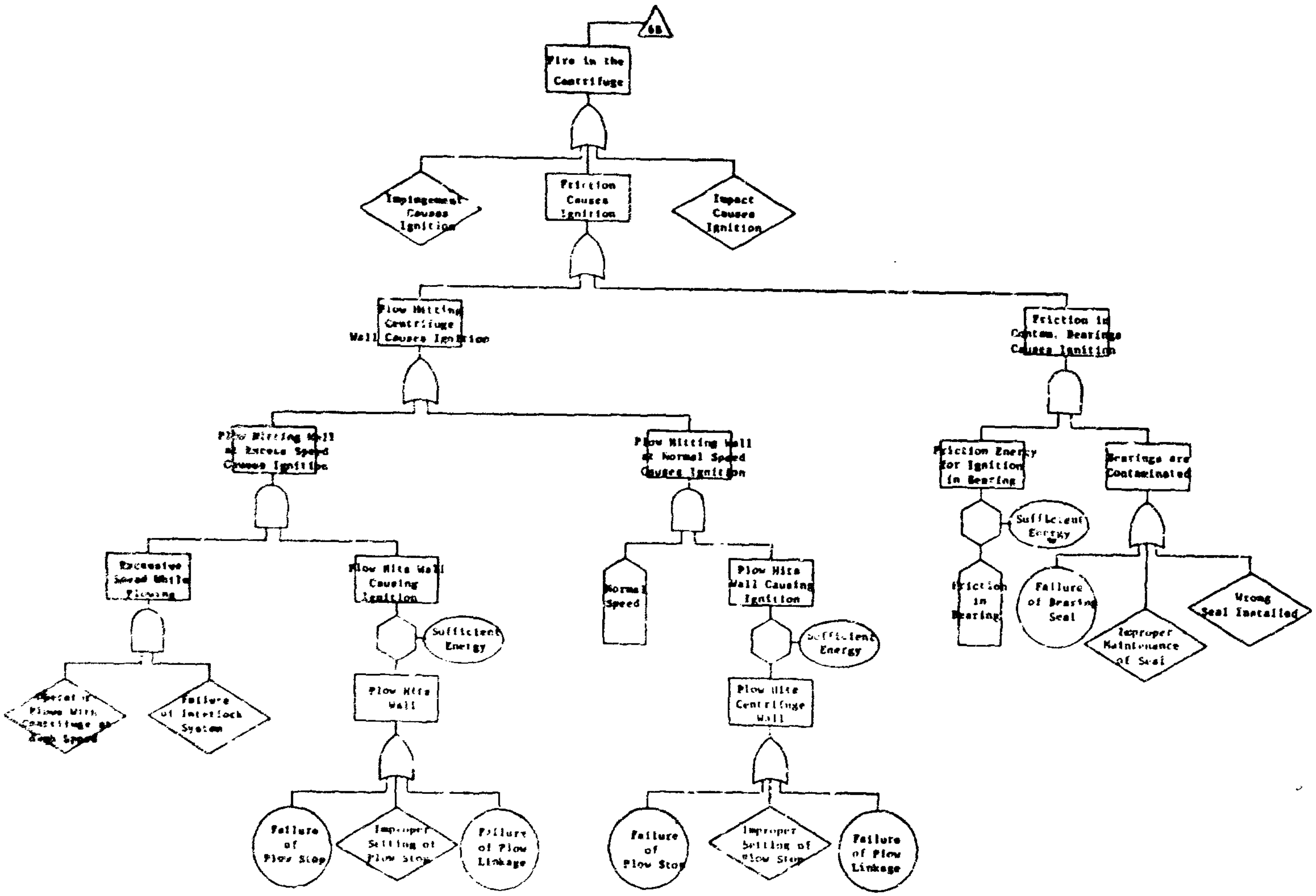

4C
Friction In Control Valve Causes Ign.
Friction In Valve Packing Causes Ign.
Friction In Valve Seat Causes Ign.
Sufficient Energy
Sufficient Energy
Valve Is Operated
Valve Is Closed

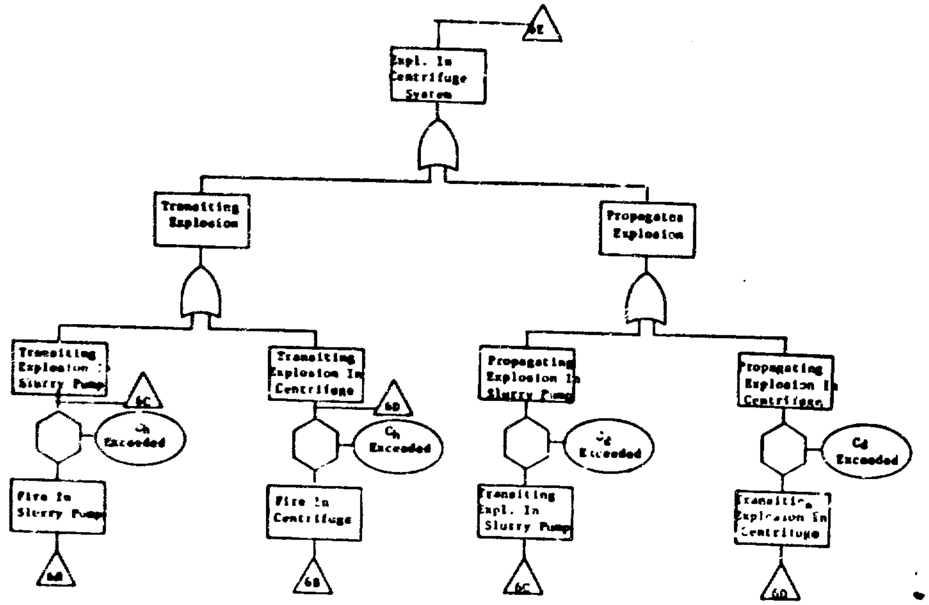

4R
Expl. In Aqueous Quench System
Transiting Explosion
Propagating Explosion
Transiting Explosion In Guolds Pump
Transiting Explosion In Quench Tank
Transiting Explosion In Control Val.
4D
4E
4F
C_h Exceeded
C_h Exceeded
C_h Exceeded
Fire In Goulds Pump
Fire In Quench Tank
Fire In Control Valve
4A
4B
4C
Propagating Explosion In Goulds Pump
Propagating Explosion In Quench Tank
Propagating Explosion In Control Valve
C_d Exceeded
C_d Exceeded
C_d Exceeded
Transiting Explosion In Goulds Pump
Transiting Explosion In Quench Tank
Transiting Explosion In Control Valve
4D
4E
4F

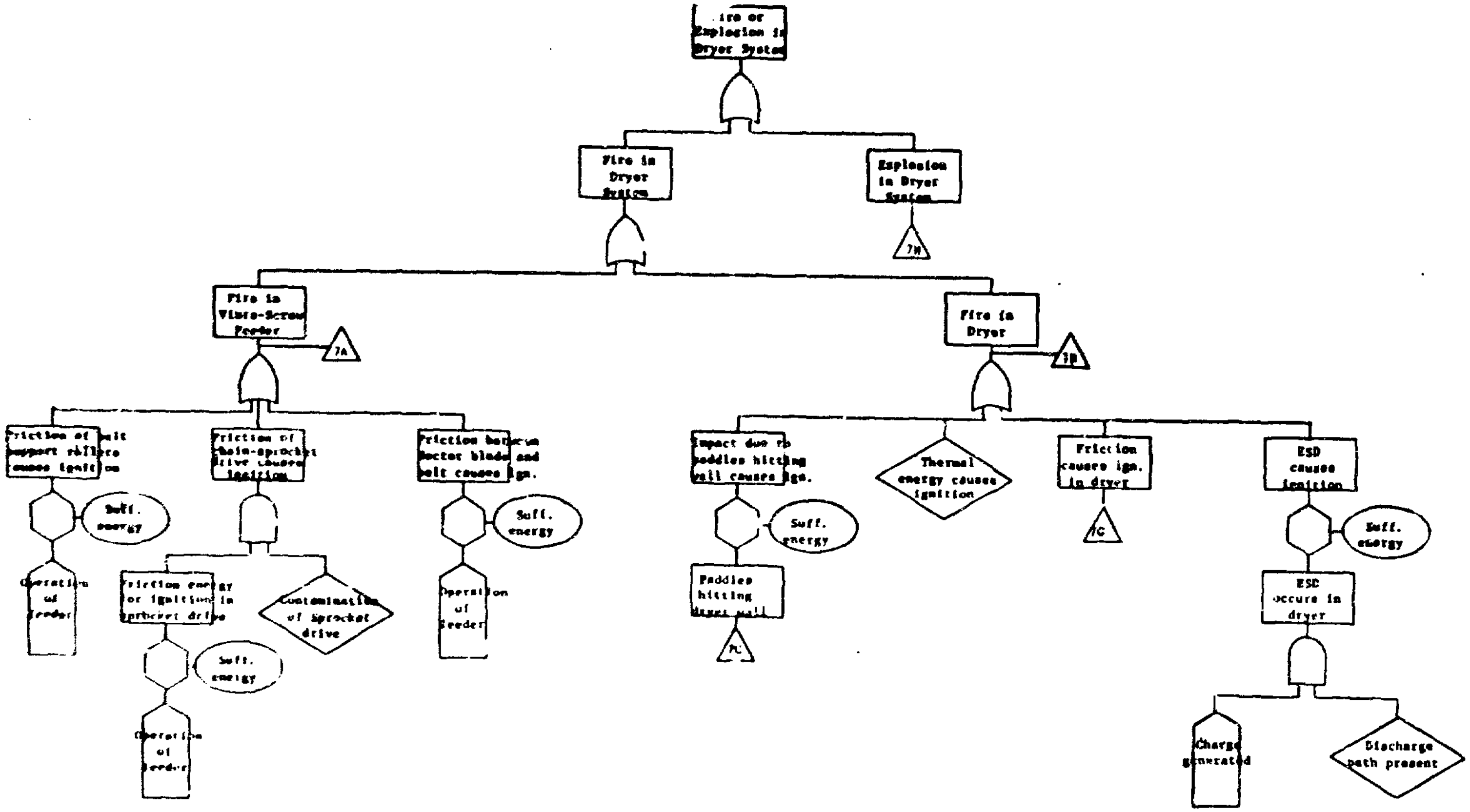

Fire or Expl. In Crystallizer System
Fire In Crystallizer
Explosion In Crystallizer System
Ign. While Mixing In Feed Tank
Ignition In Draft Tube Crystallizer
Ignition In Goulds Pump
Thermal Energy Causes Ignition
Friction Causes Ignition
ESD Causes Ignition
Impact Causes Ignition
Impeller Hits Tank Wall Causing Ign.
Friction In Contaminated Seal Causes Ign.
Impeller Hits Foreign Object Causing Ign.
Impeller Hitting A Foreign Object Causing Ign.
Impeller Hits Tank Wall Causing Ign.
Sufficient Energy
Sufficient Energy
Sufficient Energy
Sufficient Energy
Sufficient Energy
Impeller Hits Tank Wall
Friction In Contaminated Seal
Impeller Hits Foreign Object
Impeller Hits Foreign Object
Impeller Hits Tank Wall
Failure of Impeller
Failure of Bearing Retainer Mechanism
Failure of Shaft
Shaft Is Turning
Seal Is Contaminated
No Vacuum Prior to Dumping
No Vacuum During Dumping
Foreign Object Present
Crystallizer Operating
Crystallizer Dumping
Foreign Object Present
Failure of Impeller
Failure of Alignment
Failure of Shaft

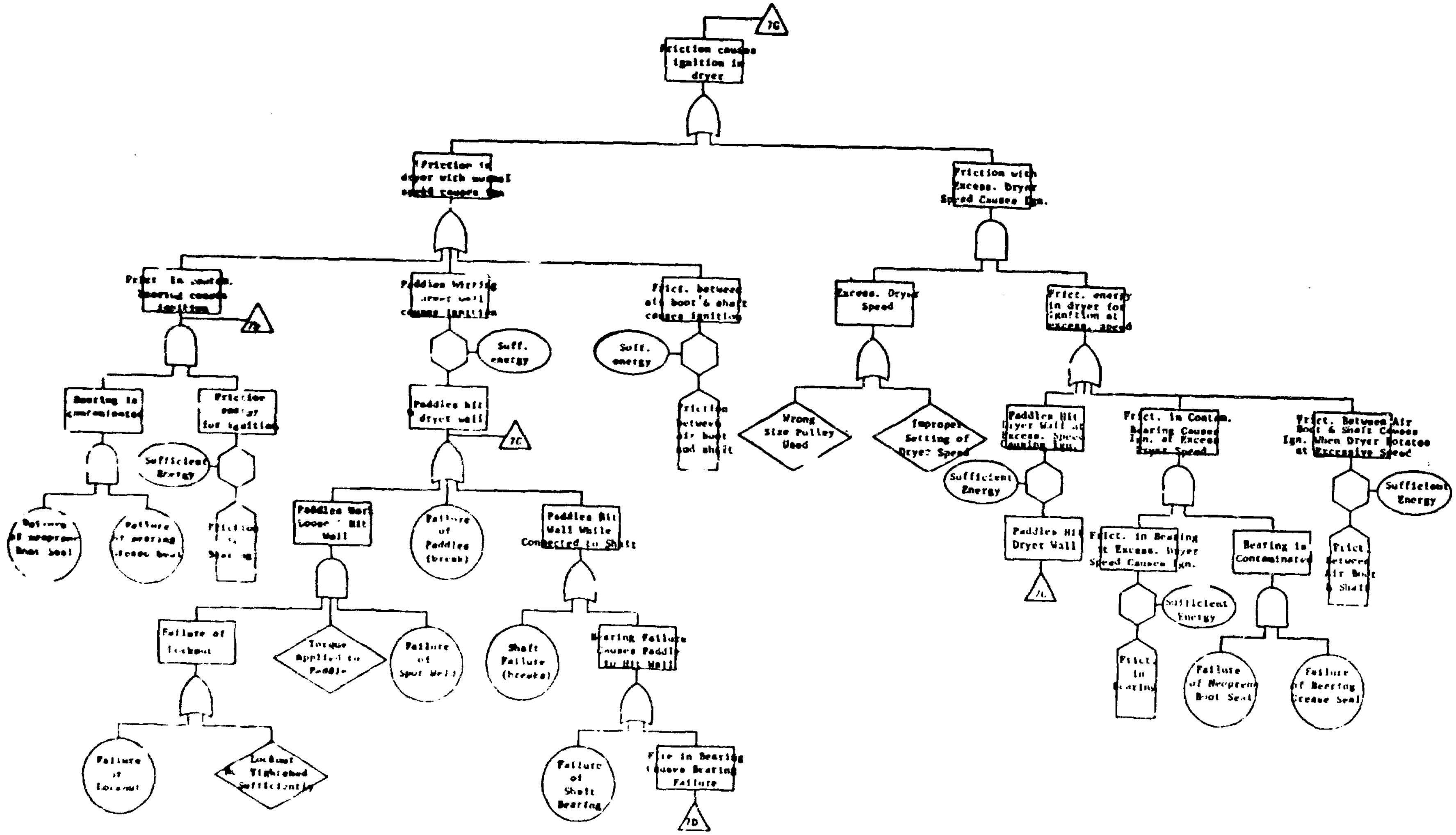

5F
Explosion In Crystallizer System
Transiting Explosion
Propagating Explosion
Transiting Explosion In Crystallizer
5C
C_h Exceeded
Fire In Crystallizer
A
Transiting Expl. In Feed Tank
5D
C_h Exceeded
Fire In Feed Tank
B
Transiting Expl. In Solids Pump
5E
C_h Exceeded
Fire In Solids Pump
A
Propagation Explosion In Crystallizer
C_d Exceeded
Transiting Expl. In Crystallizer
Propagating Explosion In Feed Tank
C_J Exceeded
Transiting Explosion In Feed Tank
5D
Propagation Explosion In Solids Pump
C_J Exceeded
Transiting Explosion In Solids Pump
5K

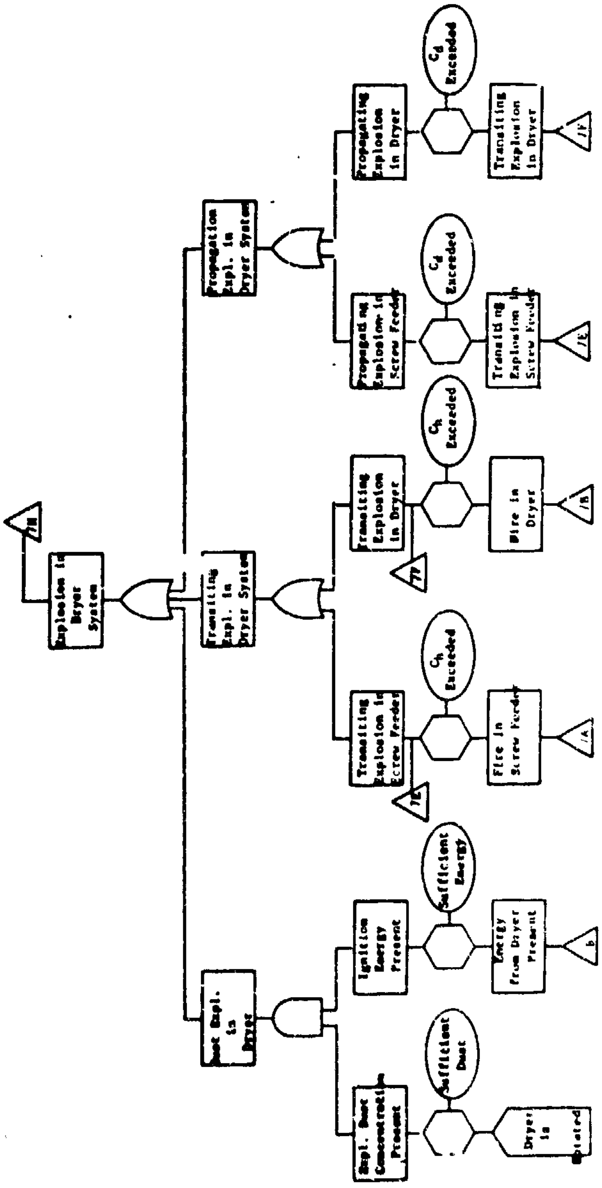

Fire or Explosion in Centrifuge System
Fire in Centrifuge System
Explosion in Centrifuge System
6Z
Fire in the Slurry Pump
6A
Fire in the Centrifuge
6B
ESD Causes Ignition
Thermal Energy Causes Ignition
Friction in Pump Causes Ignition
Impact due to Impeller Hitting Pump Case Causes Ignition
Sufficient Energy
Impeller Hits Pump Case
Failure of Shaft
Failure of Shaft Alignment Mechanism
Failure of Impeller
Impeller Hits Foreign Object Causes Ignition
Friction in Mechanical Seal Causes Ignition
Friction due to Impeller Hitting Pump Case Causes Ignition
Sufficient Energy
Impeller Hits Pump Case
Failure of Shaft Alignment Mechanism
Failure of Impeller
Improper Gasket Between Pump Fire & Housing
Failure of Shaft
Excess Friction Causes Ignition In Mechanical Seal
Normal Friction Causes Ignition in Mechanical Seal
Excess Friction in Seal Causes Ignition
Sufficient Energy
Seal Surfaces are Contaminated
6F
Seal Surfaces are Contaminated
6E
Normal Friction in Seal Causes Ignition
Sufficient Energy
Normal Friction in Seal
Material Being Pumped
Seal is Not Flushed
Blockage in Lantern Ring
No Flush to Lantern Ring
Failure of Flush Control System
No Flush to Control System
Seal Failure
Improper Installation
Improper Maintenance

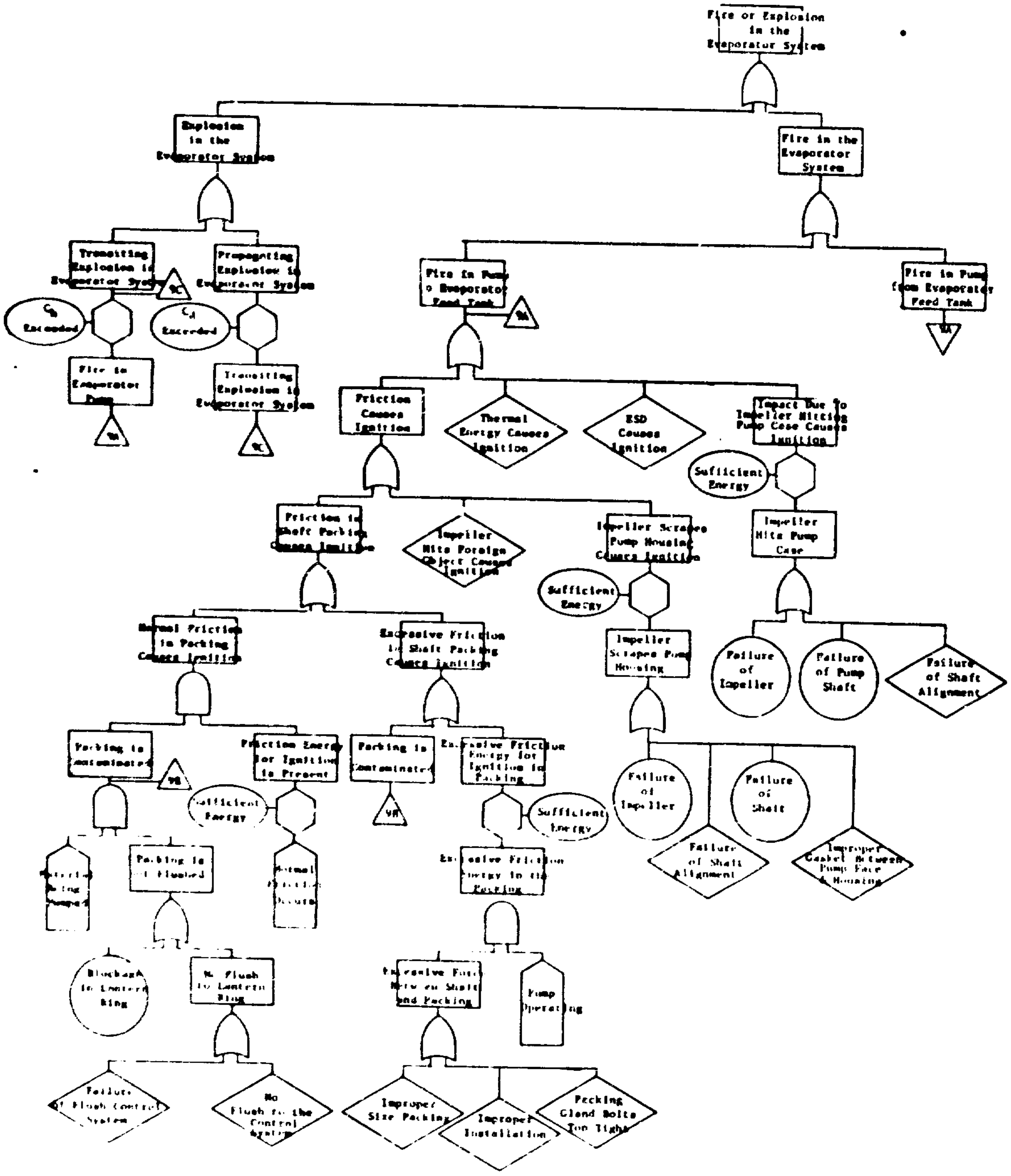

6A
Fire in the Centrifuge
Impingement Causes Ignition
Friction Causes Ignition
Impact Causes Ignition
Plow Hitting Centrifuge Wall Causes Ignition
Friction in Contam. Bearings Causes Ignition
Plow Hitting Wall at Excess Speed Causes Ignition
Plow Hitting Wall at Normal Speed Causes Ignition
Friction Energy for Ignition in Bearing
Bearings are Contaminated
Excessive Speed While Plowing
Plow Hits Wall Causing Ignition
Sufficient Energy
Plow Hits Wall
Normal Speed
Plow Hits Wall Causing Ignition
Sufficient Energy
Plow Hits Centrifuge Wall
Sufficient Energy
Friction in Bearing
Failure of Bearing Seal
Improper Maintenance of Seal
Wrong Seal Installed
Operation of Plows With Centrifuge at High Speed
Failure of Interlock System
Failure of Plow Stop
Improper Setting of Plow Stop
Failure of Plow Linkage
Failure of Plow Stop
Improper Setting of Plow Stop
Failure of Plow Linkage

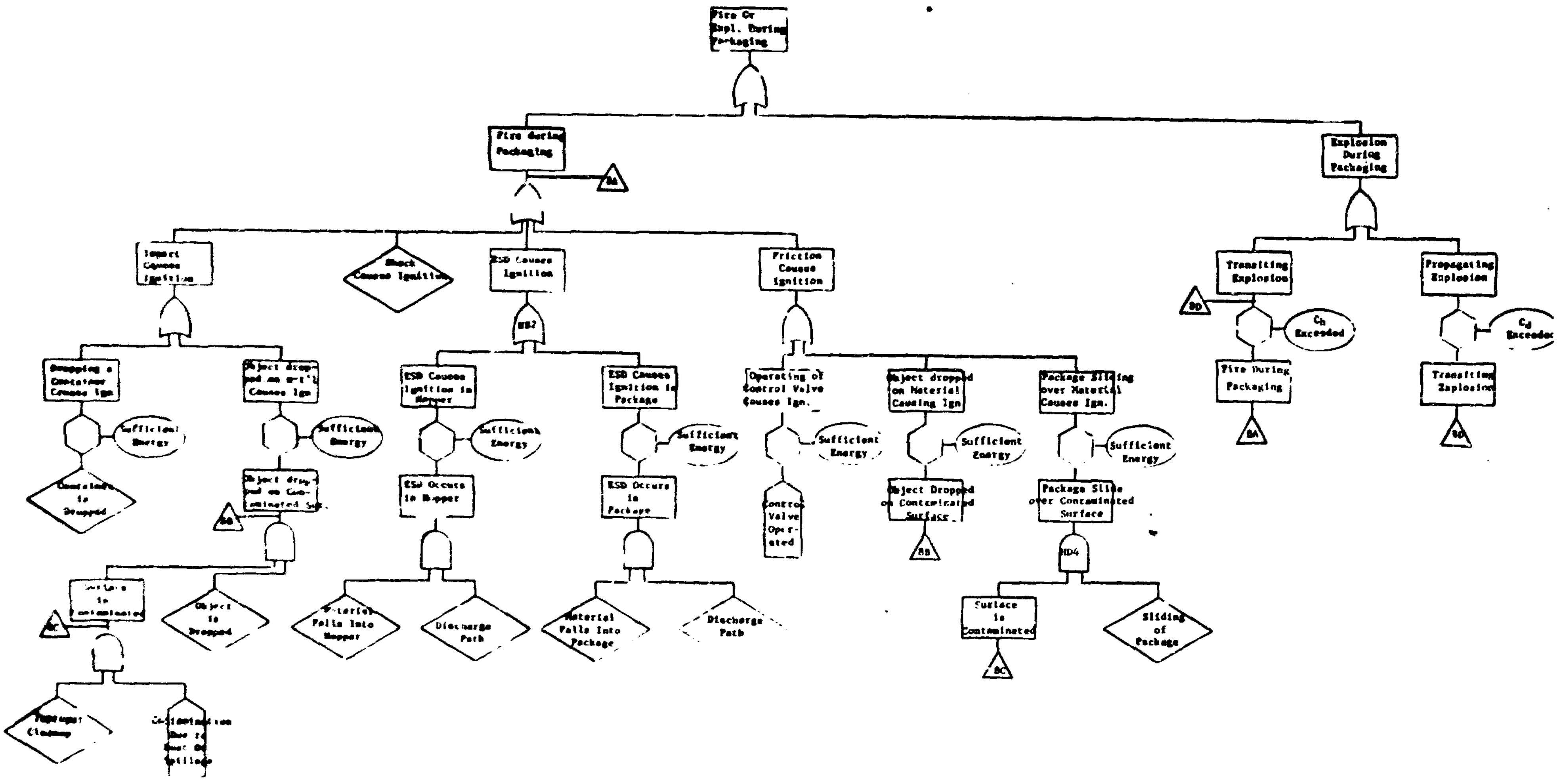

6E
Expl. In Centrifuge System
Transiting Explosion
Propagates Explosion
Transiting Explosion In Slurry Pump
6C
C_h Exceeded
Fire In Slurry Pump
6A
Transiting Explosion In Centrifuge
6D
C_h Exceeded
Fire In Centrifuge
6B
Propagating Explosion In Slurry Pump
C_d Exceeded
Transiting Expl. In Slurry Pump
6C
Propagating Explosion In Centrifuge
C_d Exceeded
Transiting Explosion In Centrifuge
6D


.ire or Explosion in Dryer System
Fire in Dryer System
Explosion in Dryer System
7M
Fire in Vibro-Screw Feeder
7A
Fire in Dryer
7B
Friction of belt support rollers causes ignition
Suff. energy
Operation of feeder
Friction of chain-sprocket drive causes ignition
Friction energy for ignition in sprocket drive
Suff. energy
Operation of feeder
Contamination of sprocket drive
Friction between doctor blade and belt causes ign.
Suff. energy
Operation of feeder
Impact due to paddles hitting wall causes ign.
Suff. energy
Paddles hitting dryer wall
7C
Thermal energy causes ignition
Friction causes ign. in dryer
7C
ESD causes ignition
Suff. energy
ESD occurs in dryer
Charge generated
Discharge path present


7G
Friction causes ignition in dryer
Friction in dryer with normal speed causes Ign.
Friction with Excess. Dryer Speed Causes Ign.
Frict. in contam. bearing causes ignition
7D
Bearing in contaminated
Friction energy for ignition
Sufficient Energy
Failure of neoprene boot seal
Failure of bearing grease seal
Friction in bearing
Paddles hitting dryer wall causes ignition
Suff. energy
Paddles hit dryer wall
7C
Paddles Work Loose - Hit Wall
Failure of Paddles (break)
Paddles Hit Wall While Connected to Shaft
Failure of Lockout
Torque Applied to Paddle
Failure of Spot Weld
Shaft Failure (breaks)
Bearing Failure Causes Paddle to Hit Wall
Failure of Locknut
Locknut Tightened Sufficiently
Failure of Shaft Bearing
Fire in Bearing Causes Bearing Failure
7D
Frict. between air boot & shaft causes ignition
Suff. energy
Friction between air boot and shaft
Excess. Dryer Speed
Wrong Size Pulley Used
Improper Setting of Dryer Speed
Frict. energy in dryer for ignition at excess. speed
Paddles Hit Dryer Wall at Excess. Speed Causing Ign.
Sufficient Energy
Paddles Hit Dryer Wall
7C
Frict. in Contam. Bearing Causes Ign. at Excess Dryer Speed
Frict. in Bearing at Excess. Dryer Speed Causes Ign.
Sufficient Energy
Frict. in Bearing
Bearing in Contaminated
Failure of Neoprene Boot Seal
Failure of Bearing Grease Seal
Frict. Between Air Boot & Shaft Causes Ign. When Dryer Rotates at Excessive Speed
Sufficient Energy
Frict. Between Air Boot & Shaft


7M
Explosion in Dryer System
Dust Expl. in Dryer
Transiting Expl. in Dryer System
Propagation Expl. in Dryer System
Expl. Dust Concentration Present
Sufficient Dust
Dryer is Operated
Ignition Energy Present
Sufficient Energy
Energy from Dryer Present
b
Transiting Explosion in Screw Feeder
7E
C_h Exceeded
Fire in Screw Feeder
1A
Transiting Explosion in Dryer
7F
C_h Exceeded
Fire in Dryer
1B
Propagating Explosion in Screw Feeder
C_d Exceeded
Transiting Explosion in Screw Feeder
1E
Propagating Explosion in Dryer
C_d Exceeded
Transiting Explosion in Dryer
1F


Fire or Explosion in the Evaporator System
Explosion in the Evaporator System
Fire in the Evaporator System
Transmitting Explosion to Evaporator System
9C
Propagating Explosion in Evaporator System
C_a Exceeded
C_d Exceeded
Fire in Evaporator Pump
9A
Transmitting Explosion to Evaporator System
9C
Fire in Pump to Evaporator Feed Tank
9A
Fire in Pump from Evaporator Feed Tank
9A
Friction Causes Ignition
Thermal Energy Causes Ignition
ESD Causes Ignition
Impact Due to Impeller Hitting Pump Case Causes Ignition
Sufficient Energy
Impeller Hits Pump Case
Failure of Impeller
Failure of Pump Shaft
Failure of Shaft Alignment
Friction in Shaft Packing Causes Ignition
Impeller Hits Foreign Object Causes Ignition
Impeller Scrapes Pump Housing Causes Ignition
Sufficient Energy
Impeller Scrapes Pump Housing
Failure of Impeller
Failure of Shaft
Failure of Shaft Alignment
Improper Gasket Between Pump Face & Housing
Normal Friction in Packing Causes Ignition
Excessive Friction in Shaft Packing Causes Ignition
Packing is Contaminated
9B
Friction Energy for Ignition is Present
Sufficient Energy
Packing is Contaminated
Excessive Friction Energy for Ignition in Packing
Sufficient Energy
Material Being Pumped
Packing is not Flushed
Normal Friction Occurs
Excessive Friction Energy in the Packing
Blockage in Lantern Ring
No Flush to Lantern Ring
Excessive Force Between Shaft and Packing
Pump Operating
Failure of Flush Control System
No Flush to the Control System
Improper Size Packing
Improper Installation
Packing Gland Bolts Too Tight


Fire Or Expl. During Packaging
Fire During Packaging
BA
Explosion During Packaging
Impact Causes Ignition
Shock Causes Ignition
ESD Causes Ignition
Friction Causes Ignition
Transiting Explosion
BD
Propagating Explosion
C_h Exceeded
C_d Exceeded
Fire During Packaging
BA
Transiting Explosion
BD
Dropping a Container Causes Ign
Sufficient Energy
Container is Dropped
Object dropped on mat'l Causes Ign
Sufficient Energy
Object dropped on Contaminated Sur.
BB
Surface is Contaminated
BC
Object is Dropped
Improper Cleanup
Contamination Due to Dust Or Spillage
HB2
ESD Causes Ignition in Hopper
Sufficient Energy
ESD Occurs in Hopper
Material Falls Into Hopper
Discharge Path
ESD Causes Ignition in Package
Sufficient Energy
ESD Occurs in Package
Material Falls Into Package
Discharge Path
Operating of Control Valve Causes Ign.
Sufficient Energy
Control Valve Operated
Object dropped on Material Causing Ign
Sufficient Energy
Object Dropped on Contaminated Surface
BB
Package Sliding over Material Causes Ign.
Sufficient Energy
Package Slide over Contaminated Surface
HD4
Surface is Contaminated
BC
Sliding of Package

APPENDIX V

LITERATURE SEARCH - RELATED TO PRODUCTION OF GUANIDINE NITRATE FROM UREA

APPENDIX V

LITERATURE SEARCH

RELATED TO PRODUCTION OF GUANIDINE NITRATE FROM UREA

by John T. Hays
Hercules Research Center

Introduction

Work in progress at Hercules Kenvil Plant and the Research Center on production of guanidine nitrate from urea led to a request for a literature search on this general subject. The objectives of this search were: to make certain that recent literature on the basic process has been covered, and to develop information relative to production of by-products and their possible effects on catalyst performance. Chemical Abstracts was thoroughly checked from 1956 through October 16, 1972 and in some areas from 1947. The information is divided into four general categories: (1) Production of guanidine nitrate from urea. (2) Reactions of urea at temperatures from 100°C. to 200°C. This subject is of interest in connection with formation of by-products in the urea-ammonium nitrate feed, which is held at about 110°C. for extended periods, and in connection with formation of by-products under the reaction conditions for production of guanidine nitrate. (3) Formation of melamine from urea. This subject is of interest because it has been an active area of research in recent years and because it represents an extension of the type of catalytic reaction involved in production of guanidine nitrate. (4) Silica-phosphate reactions. This subject is of interest because of the indications from Hercules work that the diammonium phosphate used commercially to stabilize prilled ammonium nitrate decreases the activity of the silica gel catalyst used in production of guanidine nitrate from urea.

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I. Guanidine Nitrate from Urea

Little information was located in this search which was not already available to those working on the Hercules study of preparation of guanidine nitrate from urea. Nevertheless it seems worthwhile to consider the available information to get an understanding of the factors affecting the reaction.

One of the best sources of information is a report forwarded to us through the British Embassy and Picatinny Arsenal written by F. Armstrong and R. T. M. Fraser[1]. This report not only gives new experimental work but also gives a list of 40 references.

A. Reaction Characteristics

Guanidine nitrate is formed from urea and ammonium nitrate by an unusual reaction:

$$\mathrm{2NH_2CONH_2 + NH_4NO_3 \rightarrow NH_2C(=NH)NH_2\cdot HNO_3 + 2NH_3 + CO_2}$$

The reaction occurs over a specific temperature range given as 175-225°C.[2], with 190-200°C. preferred[3], and as 160-200°C. with 180°C. giving best yields but at less than maximum rates[4]. Similar information is given by Russian workers[5]. A catalyst is required, with silica gel being preferred, although broad classes of related silica or oxide catalysts are also claimed[3-5]. Small scale batch reactions indicate an optimum ratio for urea:ammonium nitrate:silica gel of 1:1:1[3] or 2:2:1[1].

The importance of the catalyst is seen when it is realized that uncatalyzed thermal decomposition of urea gives biuret and triuret at 120-160°C.[6-9,13]. At higher temperatures, up to 200°, cyanuric acid is formed in increasing quantities[10-12,14]. Heating biuret and triuret in the presence of ammonium nitrate but with no catalyst gave cyanuric acid[15]. With silica gel, ammonium nitrate, and urea at 195°C., the main product reported was guanidine nitrate along with 5-12% ammelide and some melamine[15]. Biuret and triuret are also converted to guanidine nitrate on heating with silica gel and ammonium nitrate[3,15]. There are thus two types of urea decomposition controlled by temperature and the presence of catalyst:

Thermal which gives mainly cyanuric acid at temperatures of 160-200°. Biuret is the main product at lower temperatures (120-160°), but its formation is reversible[16,17]. Ammelide and ammeline are formed in the thermal reaction but at much higher temperatures (>250°C.)[19,20].

Catalytic, with silica gel and ammonium nitrate, at 180-200°C., gives mainly guanidine nitrate with small amounts of the triazine by-products, cyanuric acid, ammelide, ammeline, and melamine. Intermediate biuret and triuret are largely broken down under these conditions.

The action of the silica gel catalyst has thus led to formation of guanidine nitrate and small amounts of triazine byproducts at temperatures which give cyanuric acid as the main product in the straight thermal reaction.

B. Reaction Mechanism

The first step in the thermal decomposition of urea is generally considered to be[21]:

$$NH_2CONH_2 \rightarrow HNCO + NH_3$$

This is more than a hypothetical picture of the reaction, as proved by isolation of the HNCO product[21-24], direct conversion of urea to alkali cyanates[25-27], and trimerization of HNCO from urea to cyanuric acid[10-12]. Formation of HNCO allows ready formation of the products of the thermal decomposition of urea, i.e., formation of biuret and triuret by reaction of HNCO with urea and with biuret and trimerization of HNCO.

The products of the catalytic reaction require some other mechanism. One attractive scheme is dehydration of urea to form cyanamide[5, 17, 18], known to form guanidine derivatives readily:

$$NH_2CONH_2 \rightarrow NH_2CN + H_2O$$

Interaction of NH_2CN and HNCO would give ammelide and ammeline[17, 18], and cyanamide is also known to give melamine[5].

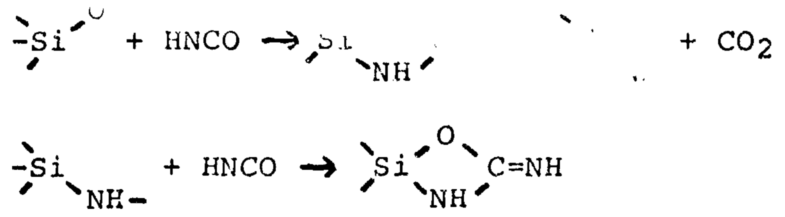
Differential thermal analysis (DTA) data were interpreted to show the presence of cyanamide in urea pyrolysis products[28], but more recent pyrolysis work has led to the conclusion that cyanamide is not a primary product of urea pyrolysis[29]. Infrared work has also led to the conclusion that formation of cyanamide is improbable[30]. Mackay[3] has stated that dehydration of urea does not occur, on the basis that carbon dioxide would have no effect if dehydration were the key reaction in formation of guanidine nitrate from urea and ammonium nitrate. Actually, he found that it was important to avoid CO_2 build-up, which led him to postulate a splitting off of CO_2. Schmidt[31], considering the analogous formation of melamine from urea, formulates it as a disproportionation of HNCO into CO_2 and carbodiimide, $C(=NH_2)_2$:

$$NH_2CONH_2 \rightarrow HNCO + NH_3$$

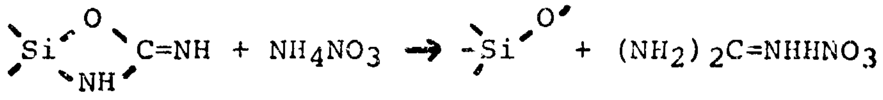
$$2HNCO \rightarrow (HN{=}C{=}NH) + CO_2$$

This would fit the observed effect of CO_2 and the unstable intermediate would give melamine on trimerization.

Schmidt[31] formulates the reaction in the fashion:



Reaction of the complex with NH_4NO_3 could then give guanidine nitrate.



The formation of guanidine nitrate would thus depend on reaction of ammonium nitrate with a catalyst complex. Molecular size of the ammonium salt reactant might be important in reaction with a complex with a specific steric arrangement. Kazarnovskii and Spasskaya[5] state that NH_4Cl and NH_4Br also form guanidine salts in this reaction but that ammonium phosphates, sulfate, carbonate, tungstate, vanadate, and salts of organic acids do not form guanidine salts in the presence of silica gel without excess pressure. The type of catalyst complex postulated could allow rationalization of this observation. The Boatright-Mackay patent[2] claims ammonium salts broadly, however.

It was also reported[5] that where best yields of guanidine were obtained with a 1:1:1 ratio of urea:NH_4NO_3:silica gel, decrease of silica gel to less than 0.8 led to formation of cyanuric acid along with guanidine salt. Thus it seems necessary to provide sufficient active catalyst sites to complex the HNCO in order to avoid the "thermal" trimerization to cyanuric acid. Blocking of active -OH groups by esterification completely deactivated the catalyst[1]. Formation of -OR groups on silica gel by this method has been reported in detail[32]. Decreasing the ammonium nitrate to stoichiometric proportions also decreases yield[5] as might be expected on the assumption that dissociation of the catalyst-HNCO complex must be avoided.

Experiments[1] with $^{15}NH_4NO_3$ and $(NH_2)_2C={}^{18}O$ showed considerable ^{15}N in the ammonium carbamate recovered but less ^{18}O than would be expected if all the CO_2 were derived from urea. The ^{15}N result suggests that the reaction: $NH_3 + {}^{15}NH_4NO_3 \rightarrow {}^{15}NH_3 + NH_4NO_3$ occurs, presumably through catalyst interactions. The loss of ^{18}O suggests exchange of surface oxygens of the catalyst through $HNC^{18}O$ in the manner postulated for the disproportionation to CO_2.

Although the specific mechanism accepted may not be critical, it is apparent that production of guanidine nitrate from urea-ammonium nitrate depends on the specific function of the catalyst to direct the reaction of the initial decomposition products of urea toward formation of guanidine nitrate and to avoid the thermal conversion of these intermediates to triazines.

Additional references on this subject were noted[33-37].

II. Reactions of Urea

The reactions of urea have been discussed in the first section as they pertain directly to the preparation of guanidine nitrate. Specific reactions will be discussed in more detail here in relation to by-product formation.

A. Hydrolysis

Hydrolysis of urea is the most important reaction of urea in the presence of water at elevated temperatures:

$$NH_2CONH_2 + H_2O \rightarrow CO_2 + 2NH_3$$

This reaction will generally be superimposed on other urea reactions if water is present. Thus the formation of guanidine nitrate:

$$NH_2CONH_2 + NH_4NO_3 \rightarrow (NH_2)\ C{=}NH{\cdot}HNO_3 + H_2O$$

becomes:

$$2NH_2CONH_2 + NH_4NO_3 \rightarrow (NH_2)_2C{=}NH.HNO_3 + CO_2 + 2NH_3$$

Hydrolysis is more rapid than biuret formation at 80°C.[38] and this is also undoubtedly true at the somewhat higher temperatures[8] (ca. 110°C.) at which the urea-ammonium nitrate feed is stored in current Hercules work on production of guanidine nitrate from urea. The hydrolysis reaction causes yield loss but reactions to form urea condensation products could cause product contamination.

General references to urea hydrolysis are listed[39-44].

B. Cyanic Acid and Cyanates

The dissociation of urea into cyanic acid and ammonia has been discussed as the first step in reactions of urea at elevated temperatures. This section will discuss references more specific to cyanic acid and cyanates.

The structure HN=C=O in straight line arrangement was indicated by Raman spectra[45]. Existence of HOCN has also been shown[49]. Hydrolysis of HNCO and NCO^- to give NH_4^+ and CO_2 and NH_3 and HCO_3^-, respectively, has been studied[46,47]

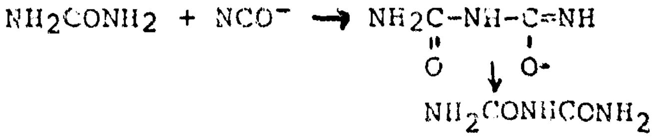
Conversion of urea to alkal metal cyanates has been cited earlier[25-27,48] as has isolation of HNCO[21-24]. Initial formation of HNCO from urea and subsequent reaction to produce biuret and triazine products will be involved in discussions of these materials in subsequent sections.

C. Biuret and Triuret

Formation of biuret from aqueous urea solutions on heating was shown[50] but this reaction was accompanied by hydrolysis.

The rate of formation of biuret from urea increases with increasing temperature up to 170°C.[7,38]. A maximum was reached initially at 200°C. after which a decrease in amount of biuret occurred[51]. At 170°C. biuret was reported to begin to decompose to urea and cyanic acid[52]. The decrease in biuret was observed at 180 and 193°C.[53] and biuret formation was reported to be reversible above the melting point, 193°C.[16,17]

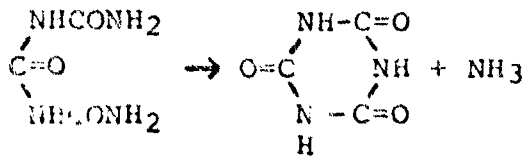
An important reference summarizes the changes which occur in the thermal decomposition of urea[30]. Infrared spectra showed that a new band appeared at 2170 cm^{-1} at the melting point of urea; it disappeared at 160° and then reappeared at 180°C., the temperature at which biuret begins to decompose. This band disappeared at higher temperatures and reappeared at the melting point of triuret. This band was assigned to cyanate ion thus deduced to be present at the melting points of urea, biuret, and triuret. Formation of the cyanate ion (or HNCO) was confirmed by amination of biuret and triuret in an autoclave at 190°C. to give urea as the sole product. HNCO was found in the gas phase over melts of all three substances. The authors suggest the following course of the reaction:



$$NH_2CONH_2 + NCO^- \rightarrow NH_2\underset{\underset{O}{\|}}{C}-NH-\underset{\underset{O^-}{|}}{C}=NH \rightarrow NH_2CONHCONH_2$$

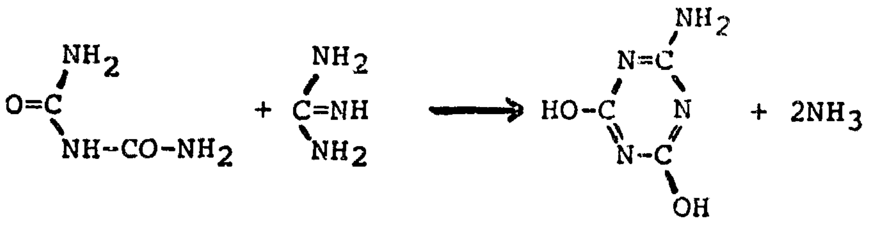
Triuret is postulated to form similarly.

Pyrolysis of triuret yielded only 15-20% of urea. It was suggested that the energetically more favorable ring closure to cyanuric acid occurs instead of complete reversal of the condensation.



triuret cyanuric acid

The reaction of guanidine with biuret to form ammelide was postulated, supported by increased ammelide yield on addition of guanidine.



biuret guanidine ammelide

Triuret is formed on pyrolysis of urea in thin films[13,56] but more readily in the presence of acid catalysts[17,54,55].

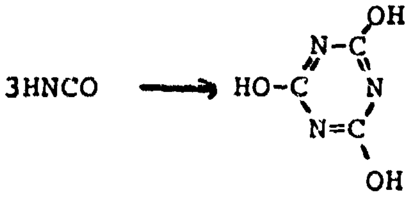
Thus any biuret and triuret formed in the guanidine nitrate process could be converted back to urea and cyanic acid; the work cited suggests the additional possibilities of conversion of biuret to ammelide and of triuret to cyanuric acid. If appreciable amounts of biuret or triuret build up in the Hercules urea-ammonium nitrate feed, there would be a possibility of yield loss by formation of ammelide or cyanuric acid. However at the temperature of 110°C., build-up of more than a few percent of biuret is unlikely[8]. Appreciable triuret would not be expected.

Processes of preparation of biuret from urea are described in a number of references[8,9,57-62]. Suppression of biuret formation in urea on storage by the use of NH_4 molybdate or $NH_4H_2PO_4$ as additives has been reported[63]. Biuret has been eliminated from urea by ammonolysis[64,65]. Urea increases the solubility of biuret in the system water-urea-biuret[66]. Biuret forms a borate with H_3BO_3[67]. Use of biuret as a fertilizer for turfgrass is described; it causes injury for a short time then is a useful source of nitrogen[68].

D. Cyanuric Acid

As stated earlier, cyanuric acid is formed by thermal decomposition of urea at about 200°C. through the trimerization of HNCO.

$$NH_2CONH_2 \longrightarrow HNCO + NH_3$$



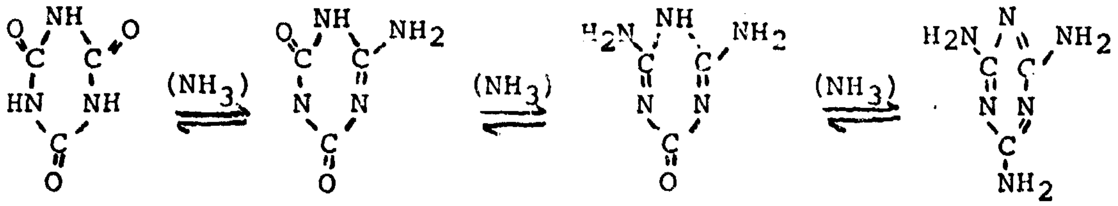
cyanuric acid

Formation of cyanuric acid is facilitated by removal of ammonia. Specific preparations involved: an ammonium halide with urea[69], H_2SO_4 as a catalyst[11,70], a phenolic solvent[10], a fluidized bed reaction[71], use of HCl to lower the partial pressure of NH_3[72], and mixtures of cyanuric acid and urea[12,14]. The reaction was carried out in vacuo at 280-300°C.[26,73] By-products, ammelide, ammeline, and melamine decreased with decreasing pressure. These by-products were stated to be formed by reaction of cyanuric acid with NH_3. This has been verified by reaction of cyanuric acid with NH_3 at 270°C./80 atm.[75]

Above 300° cyanuric acid will decompose[12]. Temperatures in the 270°-300°C. range for urea pyrolysis give ammelide and ammeline rather than cyanuric acid[19]. Temperatures above 350°C. are used in the synthesis of melamine to avoid cyanuric acid formation[74].

E. Ammelide and Ammeline

The cyanuric bases have frequently been assumed to be formed by amidation of cyanuric acid[17].



cyanuric acid ammelide ammeline melamine

These relationships can be demonstrated at temperatures of 250° and above. Ostrogovich and Bacalogu[17], however, demonstrated the independent formation of each of these triazines at temperatures in the range 160-200°C. It thus seems likely[15] that intermediates such as the postulated cyanamide, or preferably a carbodiimide complex, react to form the ammelide, ammeline, and melamine at lower temperatures.

Direct formation of ammelide and ammeline from urea at 270-300°C. is reported[19]. In pyrolysis of urea at 280-320°C., yields of ammelide and ammeline decreased with decreasing pressure[26,73]. Preparation from cyanuric acid is described[75]. Usefulness of ammelide as a slow-release fertilizer has been demonstrated[76]. Spectrophotometeric methods of analysis have been reported[77,78].

F. Ammonium Nitrate-Urea Systems

Inasmuch as a urea-ammonium nitrate feed is used for guanidine nitrate preparation, references were sought which would indicate possible effects of one component on the reactivity of the other. The system NH_4NO_3-$CO(NH_2)_2$-H_2O was studied[79]. Compounds $NH_4NO_3 \cdot CO(NH_2)_2$ and $NH_4NO_3 \cdot 2CO(NH_2)_2$ appear to exist in solution. Phase diagrams for $NH_4NO_3 \cdot CO(NH_2)_2$ were reported[80].

Addition of urea decreased the acidity of ammonium nitrate and decreased nitrogen losses 300-500%[31]. Thermal decomposition of ammonium nitrate during its preparation is reported to be inhibited by urea[82]. Urea (0.1-0.3%) added directly to HNO_3 in the preparation of NH_4NO_3 from NH_3 and HNO_3 eliminated the harmful effects of nitrogen oxides and Cl^- ions and inhibited the thermal decomposition of NH_4NO_3 during evaporation[85]. The presence of $\leq 0.7\%$ urea in NH_4NO_3 had no harmful effect on physiochemical or mechanical properties. Amounts of urea $\geq 1.5\%$ increased hygoscopicity and decreased particle strength[84].

The presence of NH_4NO_3 in the pyrolysis of urea led to an increase in the content of cyanuric acid and a decrease in the amounts of ammelide, ammeline, and melamine[83]. The effect was attributed to formation and pyrolysis of urea nitrate.

G. Boric Acid Systems

The presence of boric acid in stabilizers for ammonium nitrate led us to note references of possible interest.

In the H_3BO_3-$CO(NH_2)_2$ system, a compound was formed, $H_3BO_3 \cdot 2CO(NH_2)_2$, melting point 79.1°C.[86]

Heating 1 mole of H_3BO_3 and 2 moles of urea at about 60°C. gave a glass which decomposed above 165°C. to give BNO, stable to 1300°C. Passage of NH_3 over BNO at 500-950°C. gave relatively pure boron nitride, BN[87].

A melamine synthesis catalyst, more or less equivalent to silica gel, termed boron phosphate, was made from 100 g. boric acid and 210 g. phosphoric acid[98]. The mixture solidified on standing at room temperature and was converted to catalyst by heating to 350°C.

III. Formation of Melamine from Urea

In recent years, undoubtedly the most active area of research on reactions involving thermal decomposition of urea has been on processes for melamine from urea in eventually successful attempts to get away from dependence on calcium cyanamide and dicyanodiamide, "dicy". The first phase of this work from about 1950 to 1965 involved pressure reactions[88-99,104,105]. Then low pressure reactions were developed, first in two steps involving formation of HNCO and leading this over a catalyst[100,101,103,106,110]. Direct utilization of urea then followed[31,70,102,107,108,109,111-116].

As mentioned earlier, this reaction is analogous to guanidine nitrate production from urea, with the differences of higher temperature and substitution of NH_3 for NH_4NO_3[31,111]. Thus it utilizes a catalyst such as silica gel (also Al_2O_3, Al silica gel, and B, Al, Fe, and Si phosphates) which must contain free hydroxyl groups at high temperatures. The first step is formation of HNCO which is complexed with the catalyst. The HNCO then undergoes disproportionation to form CO_2 and the reactive carbodiimide intermediate (HN=C=NH), which trimerizes to melamine.

The initial breakdown of urea and disproportion of HNCO on the catalyst are apparently the same for the melamine and guanidine nitrate processes. Then in the guanidine nitrate process, a large excess of ammonium nitrate and a carefully controlled temperature direct the reaction of the catalyst complex to guanidine nitrate. In the melamine process, temperatures >350°C. are used. The high temperature assures completeness of the urea breakdown and the HNCO disproportionation reaction, presumably increasing the concentration of the reactive carbodiimide intermediate. The high temperature also prevents formation of cyanuric acid and ammelide. The net result is trimerization of the intermediate to melamine with only traces of by-products.

IV. Silica Gel-Phosphate Reactions

It has been determined empirically that decreases in catalyst activity observed in the course of the studies at Hercules Kenvil Plant can apparently be attributed to the presence of diammonium phosphate in the stabilizer for the ammonium nitrate used. A brief search of the literature was therefore made in an attempt to determine whether such effects are known.

No specific references were found to interactions of phosphates with silica gel in the type of system involved. There are, however, numerous references to reactions of phosphates with mineral surfaces but generally with aluminosilicates rather than silica gel. Phosphate fixation by kaolinate (an aluminosilicate) was observed and explained in terms of a two-step precipitation of an aluminum phosphate[117]. Silica-alumina gels absorbed both NH_4^+ and $HPO_4^=$ from $(NH_4)_2HPO_4$ solutions[118]. Adsorption of phosphate on kaolinite was in other examples attributed to Al or Fe[119-121].

Phosphoric acid impregnated silica showed infrared spectra attributed to phosphate interaction with surface hydroxyl groups[122]. Adsorption of orthophosphates on metal oxides was demonstrated; it was concluded that chemical bonds were formed at the reactive metal oxide sites[123]. A study of the nature of active sites concluded that silica gel acquires ion-exchange capacity and catalytic properties exclusively as a result of substitution of Al for protons in active -OH groups[124] Surface hydroxylation of silica and the nature of the groups was reported[126].

Russian workers[125] studied reaction of PCl_3 with -OH groups on silica gel at 180°C. Each PCl_3 reacted with approximately 3 hydroxyl groups, with about 90% of the surface hydroxyls being susceptible to this reaction. This reaction is the closest to the type of reaction we would postulate to explain the effect of diammonium phosphate on catalytic activity. In fact, if diammonium phosphate were as reactive as PCl_3, we would have a satisfactory explanation. However, in the present status of our information, we can only conclude that the literature is not inconsistent with surface reaction of the phosphate with -OH groups to inactivate the catalytic sites on the silica gel.

V. Summary and Conclusions

Little new information was found on the process for guanidine nitrate from urea and ammonium nitrate, but reaction characteristics and reaction mechanisms have been reviewed. The catalytic reaction with silica gel leads to the formation of guanidine nitrate and small amounts of triazine by-products at temperatures which give cyanuric acid as the main product in a straight thermal reaction. The mechanism appears to involve: (1) formation of HNCO from urea; (2) complexing of HNCO with the catalyst, followed by disproportionation to CO_2 and a reactive carbodiimide-catalyst complex; and (3) displacement of the carbodiimide by ammonium nitrate to give guanidine nitrate.

The current Hercules procedure of holding the urea-ammonium nitrate feed at about 110°C. for extended periods can be expected to involve the reactions: (1) hydrolysis of urea to give yield losses and (2) formation of biuret. An experimental check should be made of the biuret formed, but amounts in excess of 5% would not be expected. Formation of biuret is readily reversed at reaction conditions so that its formation in small amounts would not be a serious problem. Significant amounts of triazine products would not be formed at the feed temperature.

Cyanuric acid, ammelide, ammeline, and melamine can all form at the guanidine nitrate process temperature. Maintenance of catalyst activity, optimum reactant ratios, and temperatures as low as compatible with practical rates can be utilized to minimize these by-products.

Recently developed processes for production of melamine from urea and ammonia appear to involve the same initial steps as production of guanidine nitrate from urea and ammonium nitrate, namely, formation of HNCO from urea and disproportionation on the catalyst. The melamine process is run at temperatures >350°C. which avoid formation of cyanuric acid, ammelide, and ammeline and give high concentrations of the reactive intermediate which then trimerizes to melamine.

Information on possible reactions of phosphates with silica gel was sought in view of the finding at Hercules Kenvil Plant that diammonium phosphate in the ammonium nitrate stabilizer decreases the activity of the catalyst. Adsorption of phosphates on mineral surfaces has frequently been reported but generally appears to involve Al or Fe in the mineral clays. Phosphoric acid-impregnated silica showed evidence of chemical reaction of phosphate groups with surface hydroxyls. Chemical reaction between PCl_3 and hydroxyl groups of silica gel has been demonstrated and offers an analogy to what appears to happen with diammonium phosphate. Specific references have not been located for reaction of phosphates with silica gel under conditions of the guanidine nitrate reactions. However, the information in the literature is not inconsistent with surface reaction of phosphate to inactivate the catalytic sites on silica gel.

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