M-356(Book I)

OPERATING INSTRUCTIONS -- PROCESS FOR PRODUCTION OF CRYSTALLINE BORON PRODUCT 891A

By

R. D. Anderson
W. M. Bowes
E. L. Carpenter
G. I. Cathers
J. K. Dixon
K. M. Milton
B. C. Rowley
R. C. Ryder
M. Sonnino
R. T. Swain

July 1946

Work performed under Contract No. W-7401-Eng-91

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Stamford Laboratories
AMERICAN CYANAMID COMPANY
Stamford, Connecticut

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

RESEARCH LABORATORY

INVESTIGATION NO. 232
PROBLEM NO. 64
REPORTED BY R. D. Anderson, W. M. Bowes, E. L. Carpenter, G. I. Cathers, J. K. Dixon, T/3 K. M. Milton, B. C. Rowley, R. C. Ryder, M. Sonnino and R. T. Swain.
NOTE-BOOK NO. See Monthly Reports PAGES

PROBLEM STARTED February 8, 1944
PROBLEM COMPLETED June 30, 1946
PROBLEM REPORTED July 1946 √

Title of Problem

Operating Instructions for Process for Production of Product 891A at Stamford Research Laboratories, American Cyanamid Company for Manhattan District, U. S. Army Engineer Corps 1944-1946

Introduction

The Operating Instructions presented herein describe a process for producing approximately 1 kg. of Product 891A per day as constructed and operated from February 1944 through June 1946 at the Stamford Research Laboratories of the American Cyanamid Company. The research which served as the basis for this process was carried out at the S.A.M. Laboratories, Columbia University, New York, N. Y.

Code

890 = Boron trifluoride-dimethyl ether complex ($BF_3.O(CH_3)_2$).
Monomer = Dimethyl ether $(CH_3)_2O$.
Complex = Boron trifluoride-calcium fluoride complex (exact composition unknown).
Tribnol = Boron trifluoride (BF_3).
Chlorthane= Boron trichloride (BCl_3).
Tar or Trap Liquid - Thought to be largely $BF_2(OH).H_2O$.
K-Salt = Potassium fluoborate (KBF_4).
891 = Boron.
Vitamin 10 = Boron with an atomic weight of 10.
Vitamin 11 = " " " " " " 11.
"A" following a code word (e.g., 890A) refers to Vitamin 10-enriched material - that is, material in which the Vitamin 10:Vitamin 11 ratio is greater than 20:80 (the normal ratio).
"B" following a code word refers to Vitamin 11-enriched material.

362 062

QOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

Specifications for Finished Product 891A

Mesh Size. 100% to pass 100 mesh.
90% to pass 200 mesh.

Quality. 98% or better 891.
0.3% or less Fe.
Si and Ta are determined, but no limit is given on the amount, except as regards the fact that % 891 must be 98% or better.

Crystallinity. No test has been set up to determine crystallinity. This must be established by the user. Microscopical examination of 891 crystals establishes roughly that essentially all is crystalline.

Shipping Containers. Product is shipped in 1 kg. lots in friction-top tin cans.

Outline of the Process

The conversion of 890 to 891 is accomplished in four chemical steps:

1. $890 + CaF_2 \xrightarrow{50\text{-}110^\circ C.} \text{Complex} + \text{Monomer}$
2. $\text{Complex} \xrightarrow{250^\circ C.} CaF_2 + \text{Tribnol}$
3. $\text{Tribnol} + AlCl_3 \xrightarrow{100\text{-}130^\circ C.} AlF_3 + \text{Chlorthane}$
4. $\text{Chlorthane} + H_2 \xrightarrow[\text{Wire at } 1260^\circ C.]{\text{Over TaW}} 891 + HCl$

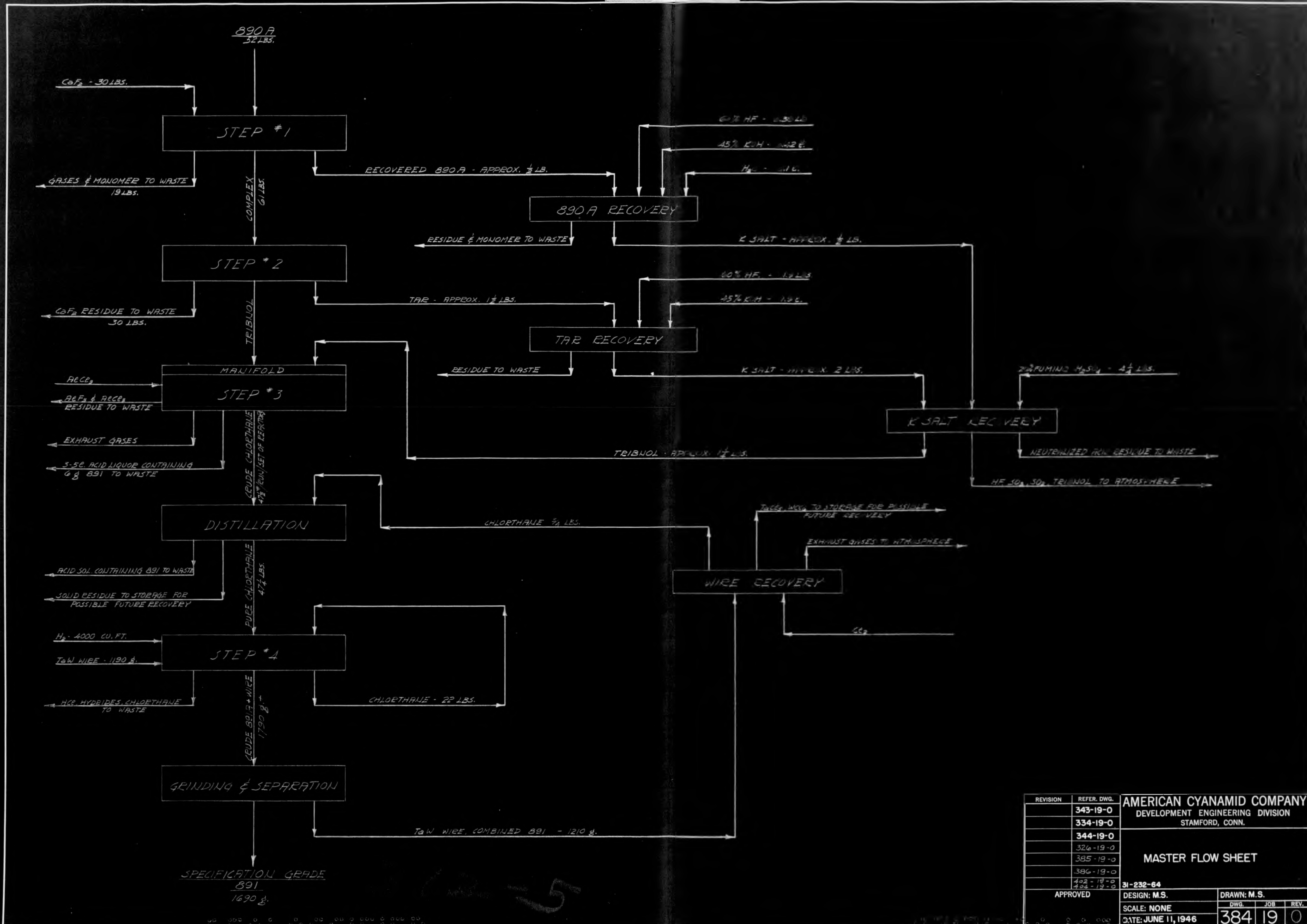
The Chlorthane produced in Step 3, however, must be distilled before use in Step 4, and in the latter step only about 50% of the Chlorthane reacts - the rest being condensed and recycled.

In Step 4 the 891 is deposited on a 94% Ta-6% W alloy wire. Hence it must be separated from the wire, ground to the proper fineness, and then separated from the iron introduced by the grinding operation, and, if necessary, from any TaW that may be present.

Three recovery processes are now also in use, and a fourth contemplated for future work. The first is a four-step process to convert liquid "Recovered 890", collected in Step 1 to Tribnol. The second, a very similar three-step process, to convert a tarry by-product formed in the second step to Tribnol. The third is used to convert the 891 which cannot be separated from the wire, or is dissolved in the wire, to Chlorthane. The fourth recovery converts the 891 previously lost in the still exit gases and residue to Tribnol.

GOF 3692A PTD. IN U. S. A.

An overall picture of the process is given by the master flow sheet. The equipment and procedure used in carrying out these operations are discussed in detail below. There will be frequent references made to the Contract No. W-7401-eng-91 Monthly Technical Reports, February 1944-June 1946, R. U. 232. Such references will be marked (Ref. 275), where 275 denotes the page number. In addition the three summary reports, A-2121, A-2122, and A-1298, file index 2.14 from the S.A.M. Laboratories, Columbia University should be used as reference reading along with the monthly technical reports mentioned above.


890 A
32 LBS.
CaF2 - 30 LBS.
STEP #1
GASES & MONOMER TO WASTE
19 LBS.
COMPLEX
61 LBS.
RECOVERED 890 A - APPROX. ½ LB.
890 A RECOVERY
RESIDUE & MONOMER TO WASTE
K SALT - APPROX. ½ LB.
STEP #2
CaF2 RESIDUE TO WASTE
30 LBS.
TRIBNOL
TAR - APPROX. 1½ LBS.
TAR RECOVERY
RESIDUE TO WASTE
K SALT - APPROX. 2 LBS.
MANIFOLD
STEP #3
AlCl3
AlF3 & AlCl3
RESIDUE TO WASTE
EXHAUST GASES
3-5 cc ACID LIQUOR CONTAINING
6 g 891 TO WASTE
CRUDE CHLORTHANE
K SALT RECOVERY
NEUTRALIZED ACID RESIDUE TO WASTE
TRIBNOL - APPROX. 1½ LBS.
DISTILLATION
CHLORTHANE ¾ LBS.
WIRE RECOVERY
EXHAUST GASES TO ATMOSPHERE
FUTURE RECOVERY
ACID SOL. CONTAINING 891 TO WASTE
SOLID RESIDUE TO STORAGE FOR
POSSIBLE FUTURE RECOVERY
PURE CHLORTHANE
47½ LBS.
H2 - 4000 CU. FT.
TaW WIRE - 1190 g.
STEP #4
HCl, HYDRIDES, CHLORTHANE
TO WASTE
CHLORTHANE - 22 LBS.
CRUDE 891 + WIRE
1790 g.
GRINDING & SEPARATION
TaW WIRE, COMBINED 891 - 1210 g.
SPECIFICATION GRADE
891
1690 g.
REVISION
REFER. DWG.
343-19-0
334-19-0
344-19-0
326-19-0
385-19-0
386-19-0
APPROVED
AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.
MASTER FLOW SHEET
31-232-64
DESIGN: M.S.
DRAWN: M.S.
SCALE: NONE
DATE: JUNE 11, 1946
DWG. 384
JOB 19
REV. 0

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

5

QOF 3692A PTD. IN U. S. A.

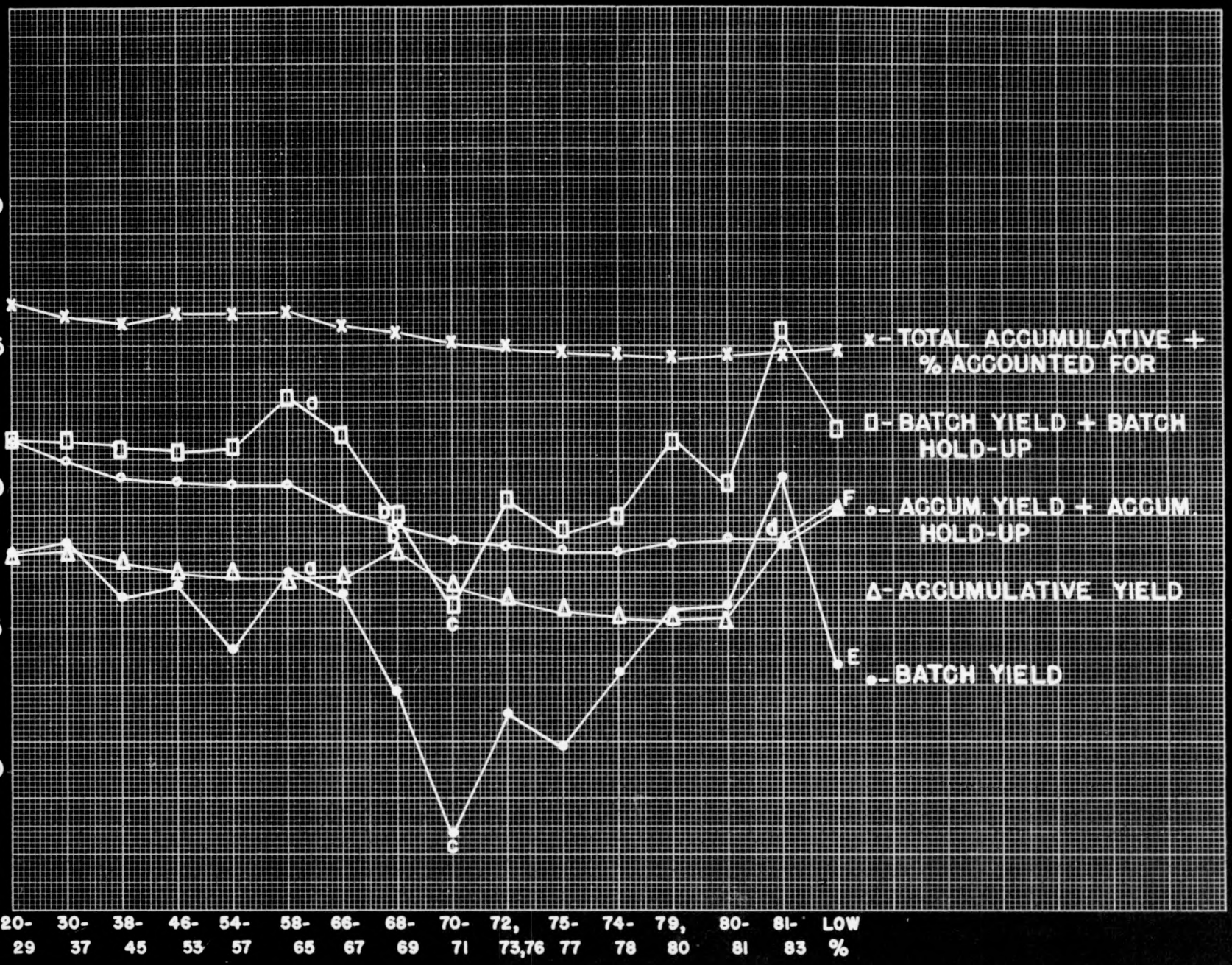
Table I

Summary of Yields[1]

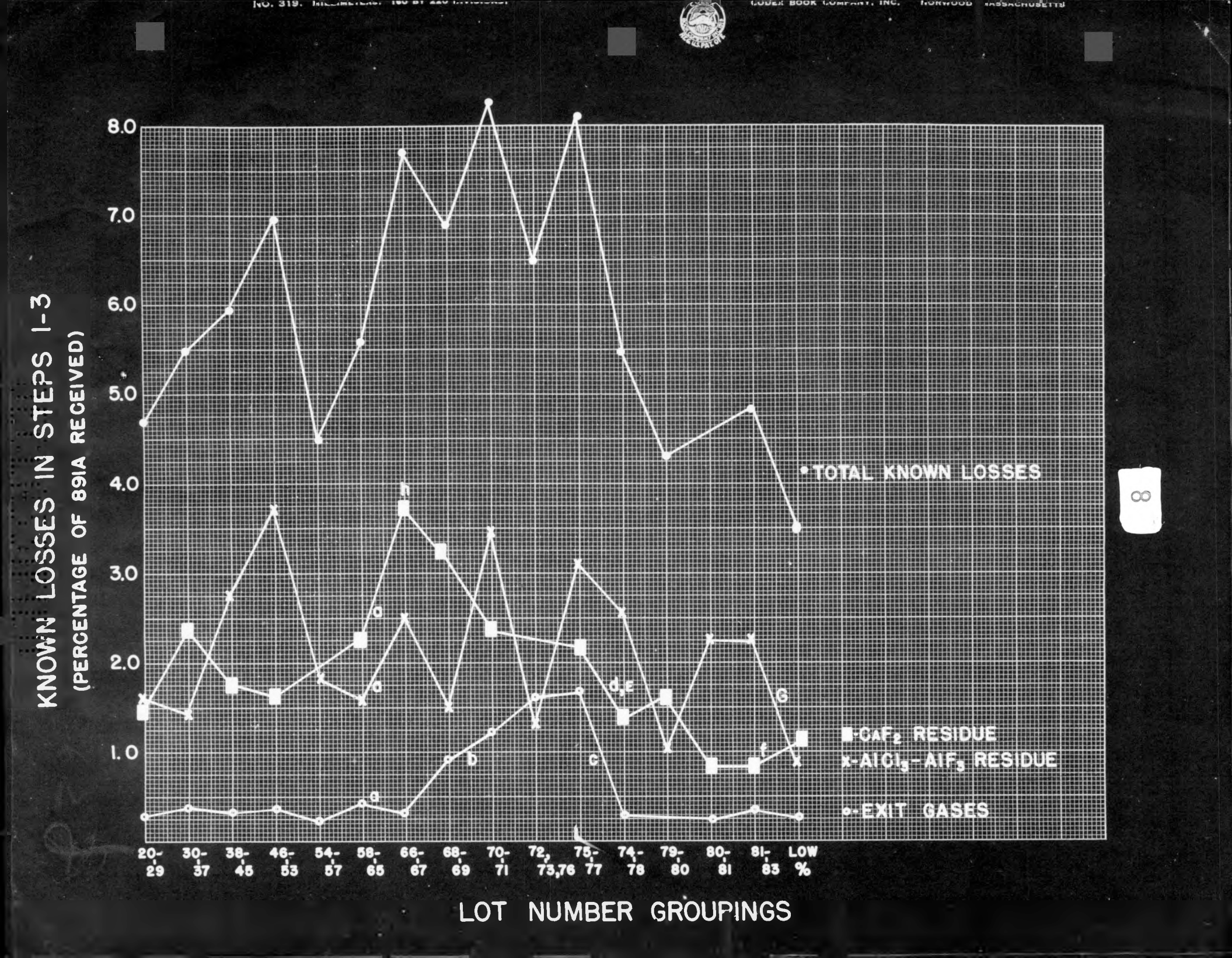
(See Dwgs., pp. 531 - 533)

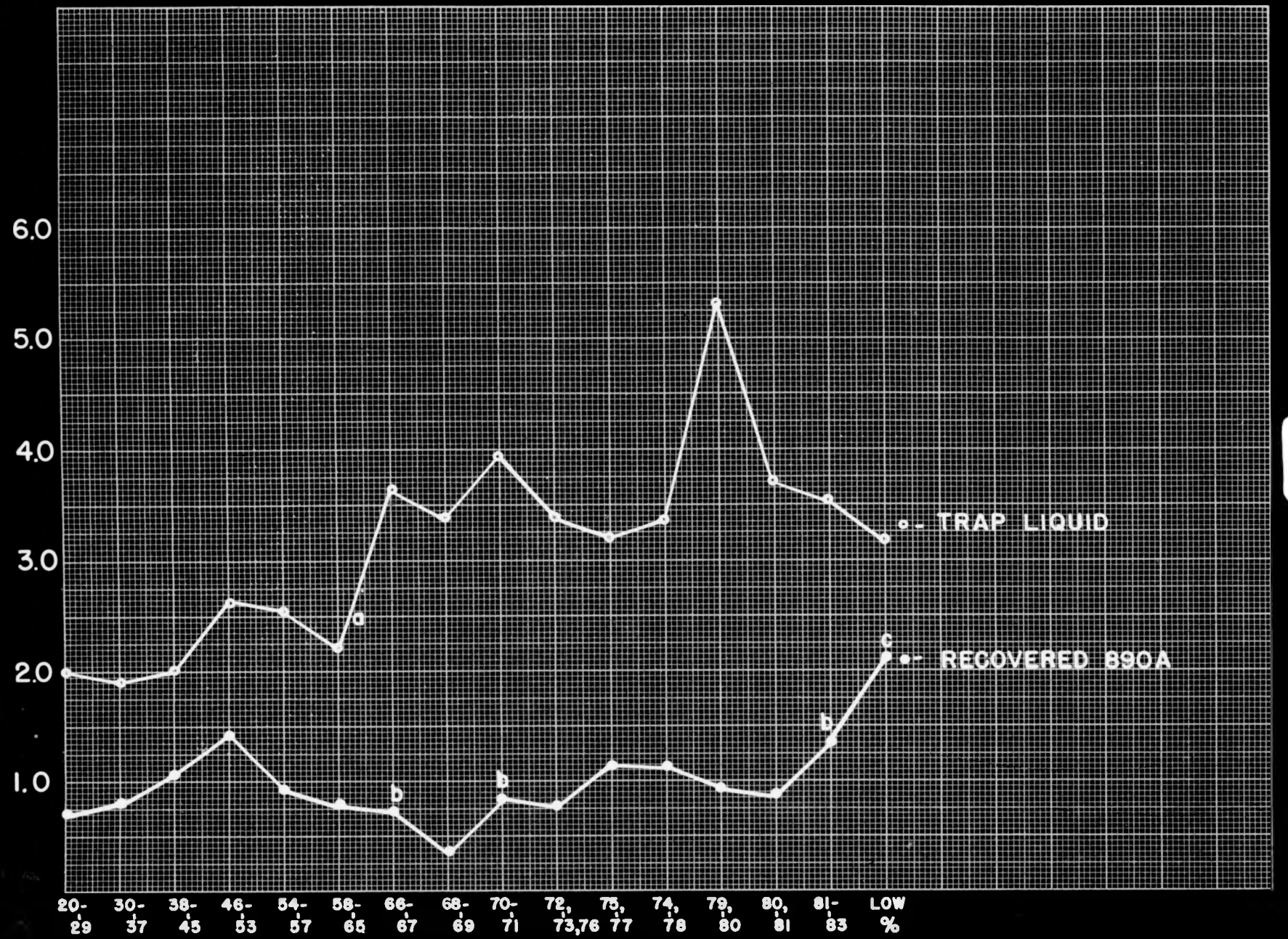
	Yield- % Theory	% Known Losses and By-Product Hold-up
Step 1	ca. 99	0.1 in Monomer 0.9 in "Rec. 890"
Steps 1-3	85.9	2.0 in CaF_2 Residues 2.2 in Column " 1.3 in Chlorthane 0.6 in Exit Gases 3.5 in Trap Liquid
Chlorthane Distillation	98.8	0.13 in Exit Gases 3.3 in Solid Residue
Step 4	97.4	2.2 in Exit Gases
Grinding and Separation	96.9	
890 and Tar-to-Salt Recoveries	92.2	
Salt-to-Chlorthane Recovery	78.4	
890 and Tar-to-Chlorthane Recovery	73.6	
Wire Recovery	ca. 98.0	
Calculated Overall Yield	82.2	
Observed Overall Yield[2]	82.5	

(1) This assumes operation over an extended period.
(2) Actual value based on 890A received and 891A shipped out.



AMERICAN CYANAMID COMPANY Investigation No. 232.
Stamford Laboratories Problem No. 64.


KNOWN LOSSES IN STEPS 1-3
(PERCENTAGE OF 891A RECEIVED)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
• TOTAL KNOWN LOSSES
■-CaF2 RESIDUE
x-AlCl3-AlF3 RESIDUE
o-EXIT GASES
20-29
30-37
38-45
46-53
54-57
58-65
66-67
68-69
70-71
72, 73,76
75-77
74-78
79-80
80-81
81-83
LOW %
LOT NUMBER GROUPINGS



AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

QOF 3692A PTD. IN U. S. A.

Table II

Raw Materials

	Name	Grade	Source	Container
Step 1	890	-	U. S. Army	5 gal. Monel cans 50-55 lbs.
	CaF_2	Reagent	General Chemical Co.	100 lb. paper bags in fibre packs.
Step 3	$AlCl_3$	Special Specs.	American Cyanamid Co. Corpus Christi, Texas	Steel drums
Step 4	H_2	Electrolytic	Am. Oxygen Service Corp., Harrison, N.J.	Trailer unit
	H_2	"	Air Reduction Co.	Cylinders-reserve
	TaW wire	6% W-94% Ta, not annealed (straight lengths, cut to 75")	Fansteel Metallurgical Corp.	Carton
Acid Treatment	HCl	6N-Technical	Stock	Bottles
Sink and Float Procedures:				
	CH_2I_2	-	Edcan Laboratories, S. Norwalk, Conn.	Bottles
	CCl_4	-	Stock	Drum
	$CHBr_2CHBr_2$	-	Dow Chemical Co., Midland, Michigan	Bottles
Recovery:	HF	60%-Technical	American Cyanamid Co.	Rubber drum
	KOH	45%-low chloride	Niagara Alkali Co.	Steel drum
	Fuming H_2SO_4	Technical	Baker Chemical Co.	Bottles
	Cl_2	-	Stock	Cylinder
Miscellaneous:				
	Dry ice	-	Dry Ice, Inc., New Haven, Conn.	Cakes
	Trichloroethylene	-	DuPont or Westvaco Chlorine	Steel drum
	Nitrogen	-	Air Reduction Co.	Cylinders
	Liquid nitrogen	-	Stamford Research Lab. of Air Reduction Company	50 l. Dewar flasks

GOF 3692A PTD. IN U. S. A.

Table III

Quantity and Usage Data

	Material	Approx. lbs. per Batch[1]	Molecular Wt.	Approximate lb. moles
Main Process	890A	51.6	ca. 113.2	0.46
	CaF_2	30	78.08	0.38
	$AlCl_3$	68	113.3	0.60
	TaW Wire	2.62	ca. 181.06	-
	H_2	4000 ($ft.^3$)	2.01	11.1
Recoveries	60% HF	1.7	-	-
	45% KOH	3.75	-	-
	Fuming H_2SO_4	4.5	-	-
	Cl_2	-	70.9	-
Approx. Yield	891A	3.75	-	-
Miscellaneous	Dry Ice	1250	-	-
	Liquid air	400 (l.)	-	-
	Nitrogen	-	-	-

(1) Assumes one batch ≈ 5 gals. 890.

Table IV

By-Products

By-Product		% 891 Recd. Contained in By-Product	Disposal
Step 1:	Monomer	0.1	Vented to atmosphere and dispersed by blower system to prevent the collection in low pockets of gases in explosive concentrations. Without elaborate apparatus, the burning of Monomer was found to be difficult and hazardous.
	Recovered 890	0.9	The 891 is recovered as Tribnol in a four-step process using H_2O, HF, KOH and fuming H_2SO_4.
Step 2:	CaF_2 Residue	2.1	Stored in fibre packs until discarded in some convenient, safe manner such as by dumping in the ocean.
	Trap Liquid	3.5	The 891 is recovered as Tribnol in a 3-step process using HF, KOH, and fuming H_2SO_4.
Step 3:	$AlCl_3$-AlF_3 Residue	2.3	Stored in steel drums until discarded in some convenient, safe manner such as by dumping on tide flats.

(continued on next page)

GOF 3692A PTD. IN U. S. A.

Table IV (con'd)

By-Products

By-Product	% 891 Recd. Contnd. in By-Product	Disposal
Distillation: Solid Residue	3.3	Dissolved and poured down the drain or crystallized and recovered in the Trap Liquid & 890 Recoveries.
Acidic aq. solns.	0.13	
Step 4: HCl	1.7	Condensed and then allowed to evaporate to the atmosphere.
Separation: TaW wire	4-5	The 891 dissolved in or adhering to wire is recovered as Chlorthane by passing Cl_2 over the wire in a quartz tube at 1000-1100°C.
Sink Fraction	0.4	Same as above.
Wire Recovery: $TaCl_5$-WCl_6	-	Stored in glass carboys until disposed of by: (1) dumping on tide flats; (2) flushing down drain; (3) or reacting with water, collecting, and selling the 891-free tantalum oxide.

GOF 3692A PTD. IN U. S. A.

References to Drawings and Photographs

This report contains numerous references to drawings and photographs, which normally will be found immediately preceding or following the reference in the text. In such cases the illustration will be mentioned by number only. When it is necessary to refer to a drawing or photograph located in another section of the report, the page number as well as the drawing number will be given.

Some of the drawings themselves contain references to other drawings, usually for details of construction. These latter drawings will be found in the section on "Equipment". Exceptions to this are the reference drawings on the "Master Flow Sheet" above, which are the flow sheets for the individual steps and will be found near the fronts on the sections on the various steps.

PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

Table of Contents

362 914

GOF 3692A PTD. IN U. S. A.

Step 4 (con'd)

GOF 3692A PTD. IN U. S. A.

GOF 3692A PTD. IN U. S. A.

Reference
List of Drawings

(continued on next page)

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

Reference
List of Drawings

Step 3 (con'd)

381-19-0	Auxiliary Equipment Step.No. 3 (Dry ice trap, receiver)	839
382-19-0	Frame for Reactors	838
223-19-2	Reducing Valves - Assembly.	582
1035/932	Trane Company Condenser	820
227-19-2	Manifold Piping	841
218-19-2	Process Piping for Reactors	579
215-19-1	Steam Piping for Reactors	843
380-19-0	Coolant Piping for Reactors	842
379-19-0	Water Piping for Reactors	844

Distillation

404-19-0	Distillation Flow Sheet	601
361-19-0	High Temperature Refrigeration System Flow Sheet	603
408-19-0	Distillation System Layout	605
407-19-0	Frame for Distillation System	606
409-19-0	Auxiliary Equipment for Distillation System - Sheet No. 1 (Kettle, Receiver, Off-Cut Receivers, Product Receiver)	607
410-19-0	Auxiliary Equipment for Distillation System - Sheet No. 2 (Distillation Tower, Weigh Tank, Dry Ice Trap, Condenser and Packing Support)	608
390-19-0	Chlorthane Bomb	671
1035/932	Trane Company Condenser	820
9309	American Marsh Pump Company Refrigeration Pump Size 41A50	823
231-19-1	Process Piping for Distillation System	609
400-19-0	Equalizer Piping for Distilling System	610
401-19-0	High Temperature Coolant Piping for Distillation System	604
412-19-0	Low Temperature Coolant Piping for Distillation System	602

Step 4

386-19-0	Flow Sheet - Step No. 4	629
266-19-0	Isolated Operation No. 2 Wiring - Step No. 4	649
387-19-0	Floor Plan - Step No. 4	681
392-19-0	Reaction Tubes	651
390-19-0	Auxiliary Equipment for Step No. 4 - Sheet No. 1 (Freezer, Filter Chlorthane Tank)	672
391-19-0	Auxiliary Equipment for Step No. 4 - Sheet No. 2 (Pre-Condenser, Pressure Blow Offs, Mixing Chamber, Chlorthane Filter)	671
393-19-0	Electrical Panel Board	666
394-19-1	Instrument Panel Board	639
395-19-0	Hydrogen Trailer	650
185-19-0	Heat Exchanger	676
188-19-1	Hydrogen Purifier	677

(continued on next page)

GOF 3692A PTD. IN U. S. A.

Reference List of Drawings

Step 4 (con'd)

200-19-0	Safety Shield	680
202-19-1	Support for Hydrogen Purifier	678
203-19-1	Sub-Zero Receiver	674
208-19-1	Sub-Zero Condenser Insulation	673
240-19-0	Sub-Zero Condenser	675
1736-B	Pittsburgh Lectro-Dryer Corporation Lectro-Dryer	679
396-19-1	Piping - Step No. 4	633
397-19-0	Piping - Step No. 4 - Sheet No. 2 (Reaction Tubes Piping)	631
398-19-0	Piping - Step No. 4 - Sheet No. 3 (Coolant Piping for Drain)	628
399-19-0	Piping - Step No. 4 - Sheet No. 4 (Coolant Piping)	666

Grinding and Separation

326-19-0	Flow Sheet for Grinding and Separation	684
329-19-0	Grinding and Separation Room Layout	711
411-19-0	Auxiliary Equipment for Grinding and Separation (Picking Tray, Receivers, Table for Stearns Magnetic Separator, Hopper for Sturtevant Laboratory Rolls)	710
21816	Sturtevant Mill Company Laboratory Rolls	704
R211	W. S. Tyler Company Ro-Tap	707
C731	Stearns Magnetic Mfg. Company Magnetic Separator	709
A-376-B	Wiring Diagram for Magnetic Separator	708

890 Recovery

385-19-0	Salt Recovery Flow Sheet	715
388-19-0	890A Recovery Equipment	714

Salt Recovery

389-19-0	K-Salt Recovery Equipment	725

Wire Recovery

402-19-0	Wire Recovery Flow Sheet	731a
403-19-0	Wire Recovery Equipment	732

Analytical

414-19-0	Analytical Apparatus	768

GOF 3692A PTD. IN U. S. A.

STEP 1

GOF 3692A PTD. IN U. S. A.

Step 1

Chemistry

When 890 and CaF_2 are mixed in the proper proportions and heated, they react to give gaseous Monomer and a solid complex of CaF_2 and Tribnol. The mechanism of the reaction is not known. The Complex is thought to consist of one molecule of CaF_2 to two of Tribnol.

$$890 + CaF_2 \xrightarrow{50\text{-}110^\circ C.} \text{Complex} + \text{Monomer}$$

While reaction of some kind takes place slowly when 890 and CaF_2 are mixed at room temperature in an open vessel, the reaction to give the Complex requires heating to carry it to completion. The mixture has been heated to 120°C. without evidence that decomposition of 890 interfered with the reaction. During the first part of the reaction the rate of evolution of Monomer is a rather sensitive function of the temperature; in the later phase of reaction, the rate is very slow even when the temperature is raised (Ref. 86 - Note again this is page 86 in the series of American Cyanamid's monthly reports, R. U. 31-232-64).

Variation of the molar ratio CaF_2:890 from 0.8:1 to 3.0:1 has little effect on the course of the reaction and practically no effect on the overall yield in the first two steps. (S.A.M. report A-2121 and Ref. 475).

The normal yield in the reaction, as measured by the amount of Monomer collected, is about 95%. Measured by the weight of the Complex obtained, it is 97-99%.

Table V

Properties of Materials in Step 1

Material	State in Which Encountered	Mol. Wt.	Apparent Density g.cm.-3	Remarks
890	Liquid	113.2	1.232 25°	Corrosive, irritating fumes in air.
CaF_2	Powder	78.08	ca. 0.8	-
Complex	Powder	-	ca. 0.7	Burns on contact with skin.
Monomer	Gas condensing at -23.65°C.	46.07	0.00209 20° 0.75 -27°	Inflammable, explosive.

Table VI

Usage Figures for Step 1

	15-Gallon Dough-Mixer	5-Gallon Dough-Mixer
Wt. 890 lbs.	51.6[1]	25.8
Wt. CaF_2 lbs.	30.0[1]	15.0
Approx. vol. of mixture	10 gal.	5 gal.
Monomer (Theor. Wt., lbs.	20.9	10.4
Monomer (Usual % Yield	93-96	93-96
Complex (Theor. Wt., lbs.	60.7	34.1
Complex (Usual % Yield[2]	97-99	97-99
Recovered 890 lbs.	0.50	0.33

(1) Mixer will readily handle a double charge.
(2) Based on weight of all material left in mixer after evolution of Monomer.

Equipment

The equipment for Step 1 is located in the extension built on the north side of the building. (See floor plan Dwg 290 A-A.) It consists of two units identical except for the size of the various elements of the unit. Flow sheet #1 (Dwg 343-19-0) depicts the larger of the two units, but except for sizes and weights is equally applicable to the smaller.

80'-0" out to out steel frame

10'-0" | 10'-0" | 10'-0" | 10'-0" | 10'-0" | 10'-0" | 10'-0" | 10'-0"

8'-0" | 8'-0"

30'-0" out to out steel frame

10'-0"

20'-0"

8'-0"

3'-0" x 7'-0" metal

3'-0" x 7'-0" metal

24 ga. corr. galv. (partition)

instrument panel bd.

CONC. FLOOR

GUTTER

4'-0"

sliding door

stone-wall board

4"x4" studs 2'-0" c.c.

2"x10" planks

stone-wall board

GUTTER

2'-0"

2'-0"

24 GA CORR. GALV. (partition)

shower

toilets

basins

urinal

4'-0"

4"x4" stud

2"x4" stud

stone-wall board

4"x4" stud

3'-0"

sliding door

CONC. FLOOR

GUTTER

3'-0" x 7'-0" metal

3'-0" x 7'-0"

3'-0" x 7'-0" metal

8'-0"

10'-0" | 10'-0" | 10'-0" | 10'-0" | 10'-0" | 8'-0" | 10'-0" | 10'-0"

80'-0" out to out steel frame

FLOOR PLAN

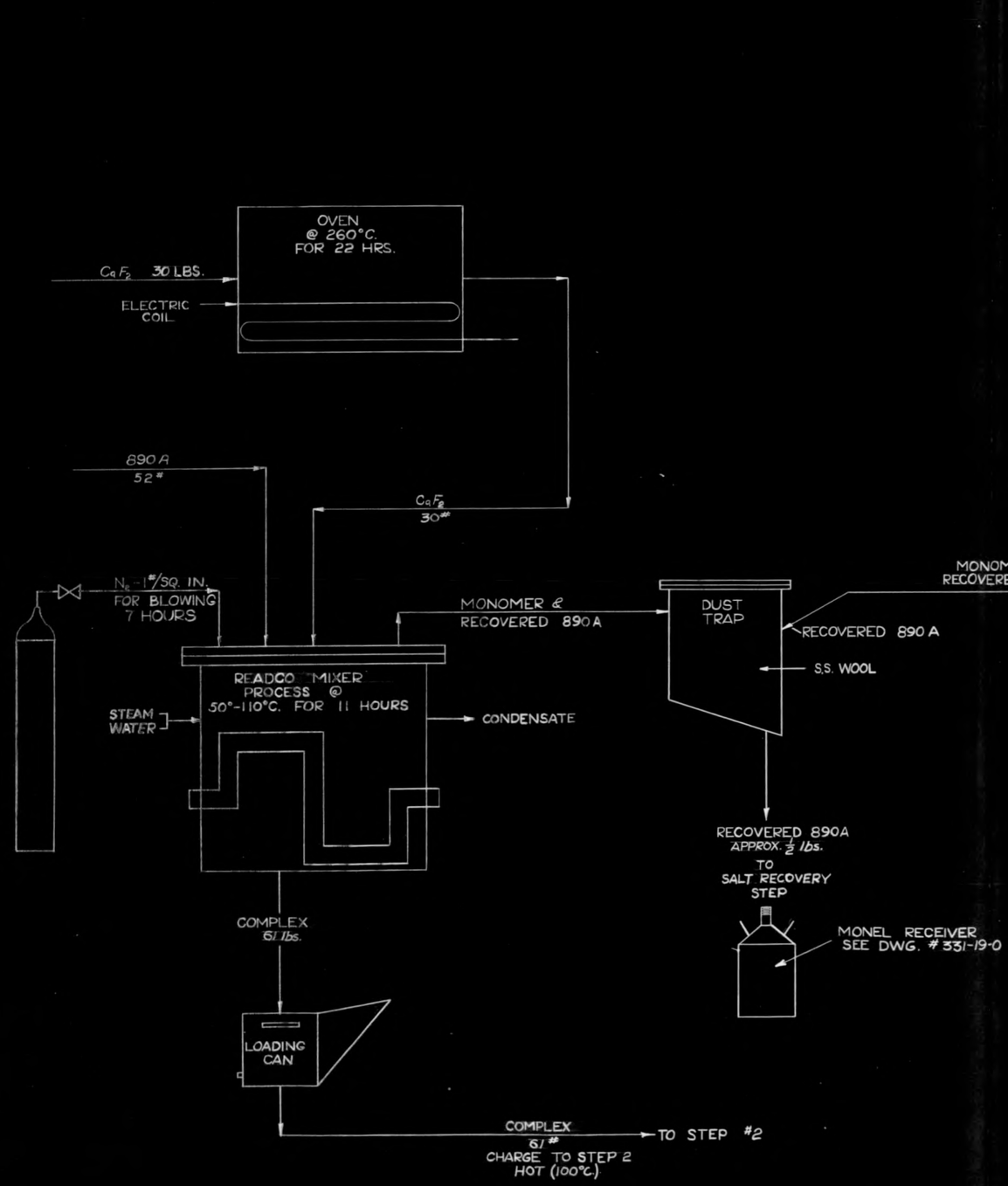
290 A-A

AMERICAN CYANAMID COMPANY
STAMFORD, CONN.

ISOLATED OPERATION BLDG No 2.

BLDG 22

	Made	Date	CV'd.	Date	App'd.	SCALE-
Original Issue						1/4"=1'-0"
Rev. No. 1		8-14-44	A.R.C.	8-15-44	CPK	JO-
Rev. No. 2						
Rev. No. 3						
Rev. No. 4						S-



REVISION	REFER. DWG.
	349-19-0
	350-19-0
	351-19-0
	358-19-0
	331-19-0

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

FLOW SHEET #1

31-232-64

DESIGN: M.S. DRAWN: W.L.

SCALE: NONE

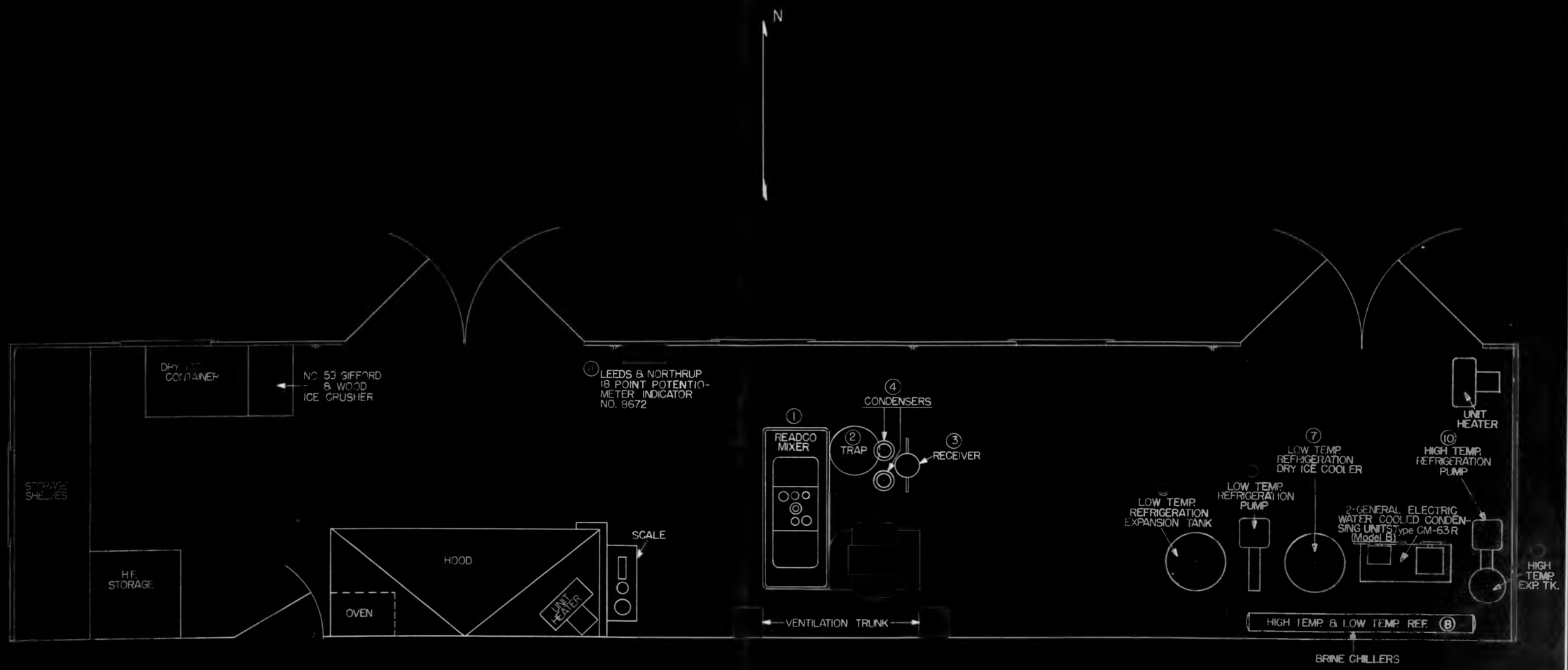
DATE: 2-5-46

DWG.	JOB	REV.
343	19	○

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

24



EQUIPMENT LIST

(1) READ MACHINERY CO. 15/32 D/A NON-VAC. MIXER DWG. NO. D-45600, D-45559, D-40425, C-40221

(2) DUST TRAP SEE DWG 358-19-0

(3) LIQUID MONOMER RECEIVER SEE DWG 356-19-0

(4) ONE WATER COOLED AND ONE LOW TEMPERATURE CONDENSERS SEE DWG 351-19-0

LOW TEMPERATURE REFRIGERATION EXPANSION TANK SEE DWG. 349-19-0

(6) AMERICAN MARSH PUMP CO. TYPE V TURBINE PUMP SIZE 41A50 DWG. W9309

(7) LOW TEMPERATURE REFRIGERATION DRY ICE COOLER SEE DWG. 349-19-0

TWO TRANE CO. 6⅝" O.D. x 84" LG. ¾" TUBE BRINE CHILLERS DWG. 1035-936

(9) HIGH TEMPERATURE REFRIGERATION EXPANSION TANK SEE DWG. 361-19-0

(10) AMERICAN MARSH PUMP CO. TYPE V TURBINE PUMP SIZE 41A50 DWG. W9309

(11) LEEDS & NORTHRUP 18 POINT POTENTIOMETER INDICATOR NO. 8672. FIVE POINTS USED.
1. TO BRINE COOLER FOR HIGH TEMP. REFRIGERATION.
2. COOLANT LINE FROM MONOMER RECEIVER.
3. WELL IN MONOMER RECEIVER.
4. LOW TEMP. CONDENSER.
5. FEED TO DOUGH MIXER.

REVISIONS	SHEET DWG.
	343-19-0
	349-19-0
	351-19-0
	358-19-0
	361-19-0
APPROVED	

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

STEP NO. 1 LAYOUT

31-232-64

DESIGN: M.S. DRAWN: wel
SCALE: 6"=1 FT.
DATE: 4/17/46

DWG.	JOB	REV.
350	19	0

36-25

AMERICAN CYANAMID COMPANY
Stamford Laboratories

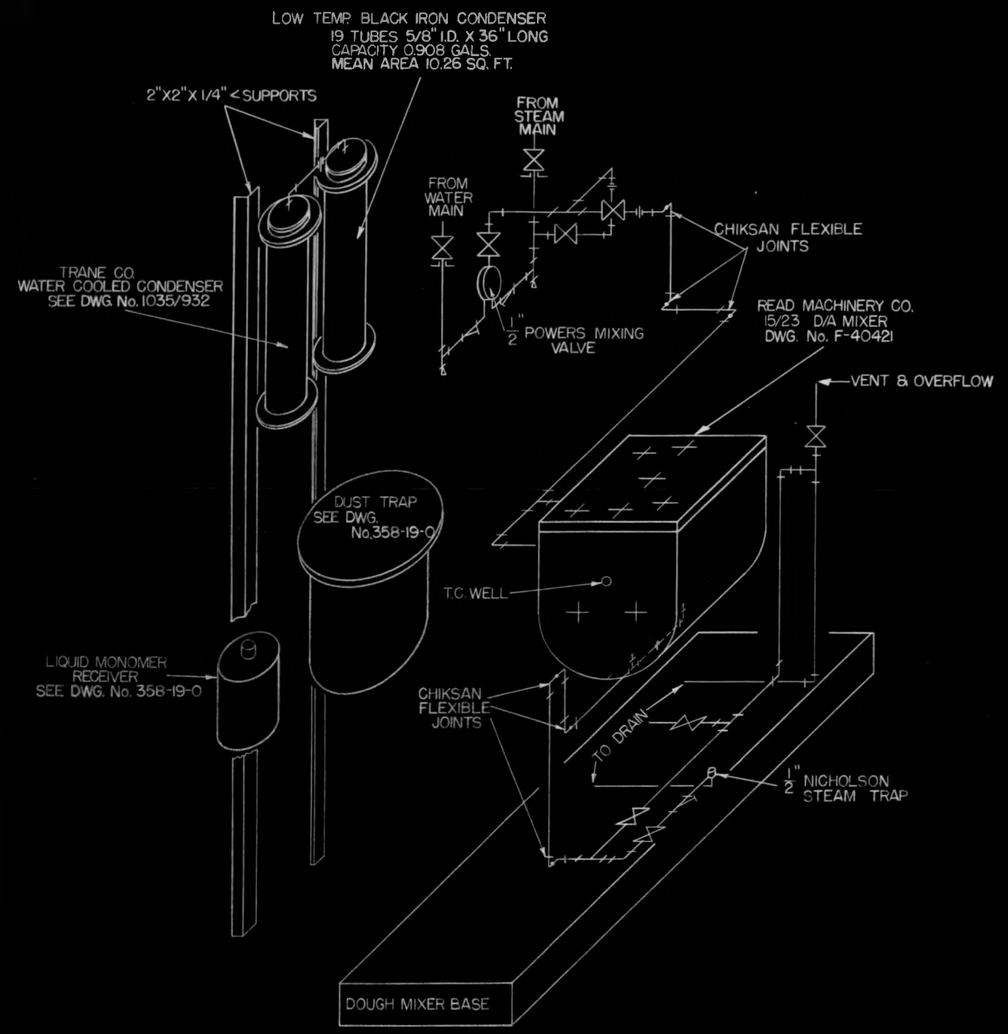
Investigation No. 232.
Problem No. 64.

DECLASSIFIED

GOF 3692A PTD. IN U. S. A.

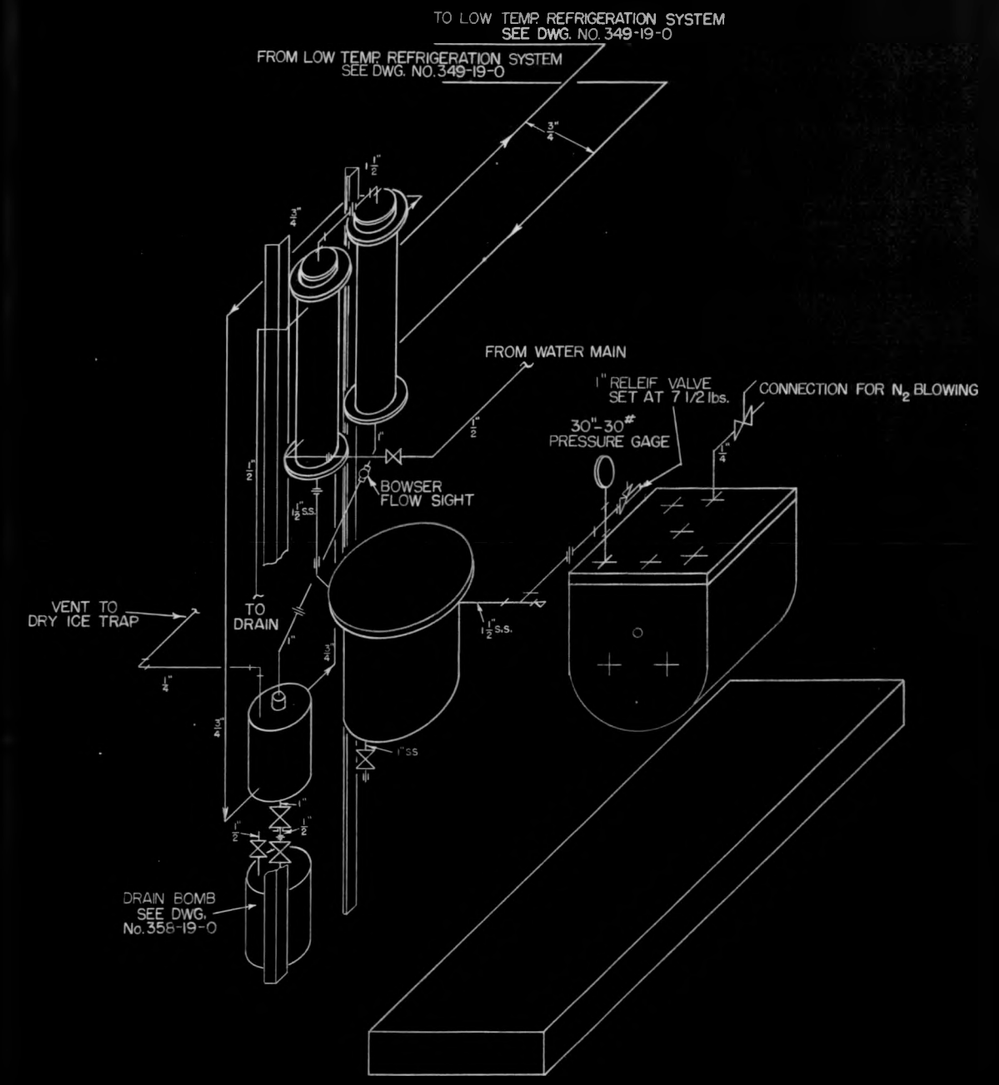
The CaF_2 and 890 are mixed and heated in the doughmixer; Monomer is given off carrying with it some powder and 890. The powder is caught on stainless steel wool in the trap, and the 890 is condensed in the 18° condenser and drained back into the trap. The Monomer is condensed in the -40° condenser and collected in the receiver except for a small fraction which is caught in the dry-ice trap or escapes into the duct system. The Complex and excess CaF_2 remain in the doughmixer as a powder.

The doughmixers are heated by mixed steam and water. The first condenser is water cooled, while the second is cooled by circulating trichloroethylene at -40°C. The trichloroethylene is cooled by two parallel systems (Dwg 349-19-0): a Freon refrigerated brine chiller and a dry ice-solvent cooled brine chiller. The Freon system alones does not have the capacity required during the period of greatest reaction and is reinforced with the other system. This consists merely of a barrel containing several coils through which the trichloroethylene is circulated. The coils are cooled with a mixture of dry-ice and trichloroethylene. The insulated barrel is shown in the center of the photograph below. In the foreground are the trichloroethylene expansion tank and the circulating pump, and on the floor in the rear, the Freon compressor. Its brine chiller is hidden behind the barrel. The temperatures are read on a Leeds and Northrup indicator mounted on the north wall near the door. Additional information and drawings of the equipment will be found below in the construction section.



STEAM, WATER, CONDENSATE DRAIN
PIPING ARRANGEMENT FOR DOUGH
MIXER BOWL

ALL PIPING 1/2" I.P.S. BLACK IRON PIPE. ALL
VALVES 1/2" BRONZE GLOBE



PROCESS, COOLANT & COOLING WATER
PIPING ARRANGEMENT

ALL PIPING BLACK IRON EXCEPT WHERE INDICATED. ALL
VALVES BRONZE GLOBE

	AMER. DWG.
	343-19-0
	349-19-0
	350-19-0
	358-19-0
APPROVED	

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

STEP NO. 1 — PIPING

31-232-64

DESIGN: M.S.
SCALE: 1" = 1 FT.
DATE: 4/13/46

AMER. DWG. 351 | 19 | 0

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

28

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

C-40398
A-36096
A-36065
40407-Va.5
B-40403
S.K.F. No. 22610A - 2 Reqd.
A-40423 - 2 Reqd.
Garlock Klozure No 1205 - 2 Reqd.
D-45589
B-27401 - 4 Reqd.
C-45591 - 2 Reqd.
B-27402A - 4 Reqd.
B-27403 - 4 Reqd.
A-40401 - 24 T 3 DP 2 Reqd
D-36050
C-40407E - 2 Reqd.
B-36059
A-36067
A-23473
A-36068
Nice #1017-2 Reqd.
A-36090-2 Reqd.
D-40396 Rear
D-40396 Front
B-36061
C-40407-6 - 4 Reqd.
A-36064
S.K.F. No. NUM45
D-45558
D-45590
C-40407-2
Garlock Klozure No 1654
S.K.F. No. 22518A - 2 Reqd.
Garlock Klozure No 2255 3 Reqd.

FOUNDATION PLAN

A-23173A
A-23175
2 Reqd.
D-45559
C-45553
G.E. "CR9440-HA" Limit Switch
A-45206
C-45592
A-45503 Thermometer Ferrule
Louis Allis Co.
15 HP. 700 R.P.M.
Explosion Proof Motor
Type EX Frame 405
Class 3F
With Sliding Base
A-45597
A-26458
C-40221
D-40425
62" Approximate

A-23172A
A-23175
2 Reqd.
B-46909 - 4 Reqd.
A-44671
A-40411
D-45589
B-36058
C-36052
B-27513B
A-45205
C-45553
D-45559
D-45590
A-40411
C-45592
D-36050
D-40425
6'-9" Approximate over all
C-40402
B-36058
C-36055
B-36092 - 75 T 5/8 DP
Morse Chain Co.
Dwg. No. D-43771
15 HP with oil tight case. 23 T Motor Pinion 79 T Driven Sprocket
B-36062
A-36063
Garlock Klozure 1360
A-36097A
S.K.F. No. NUM 55
A-36093 - 15 T 5/8 DP
S.K.F. No. NUM 45
B-36061
A-36064
D-36054

362-028

Finish Symbols: Rough Grind, Disc Grind, Coarse Polish, Fine Polish, Rough Machine, Finish Machine, Ground Finish	Scale 3 F.F. Size	READ MACHINERY CO., INC. York, Pa.	
	Date 6-20-44	General Assembly	
	Drawn By GGE		
	Checked By		
Order No.	Approved By	Equipment 15/20 D/A Non-Vac Mixer	
Material	Patt No.	Dwg. No. D-45600	

Final Print

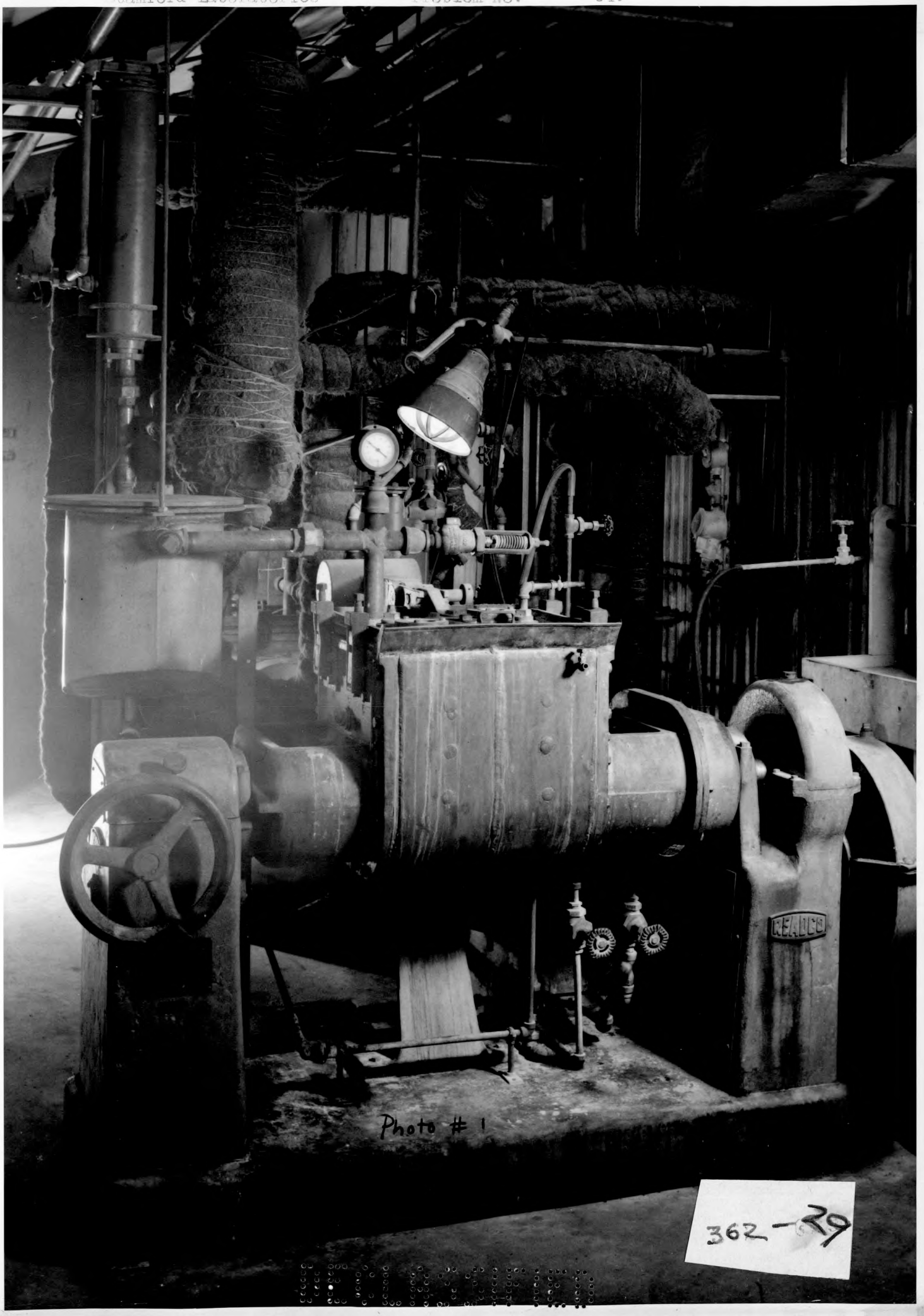


Photo # 1

362-29

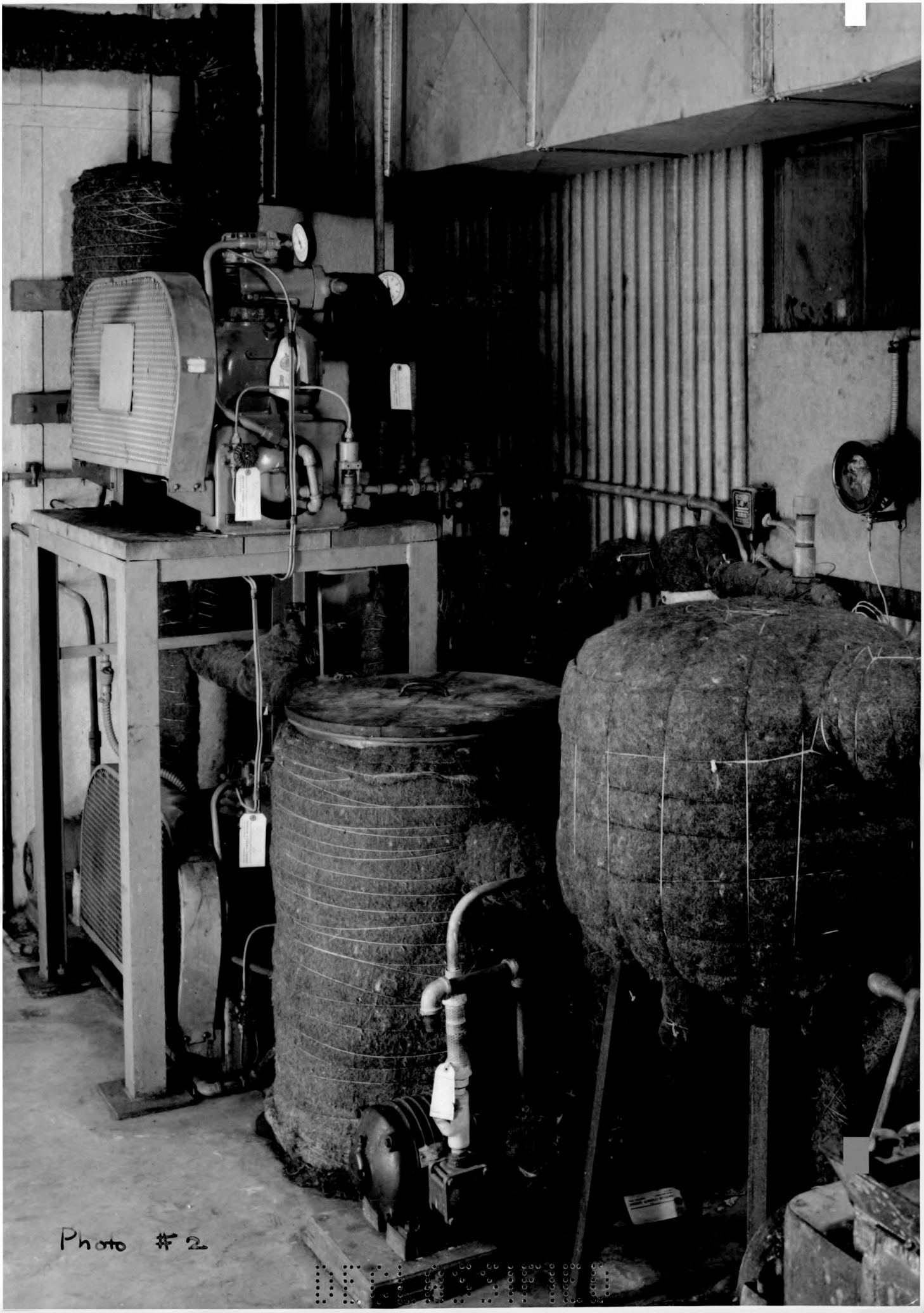
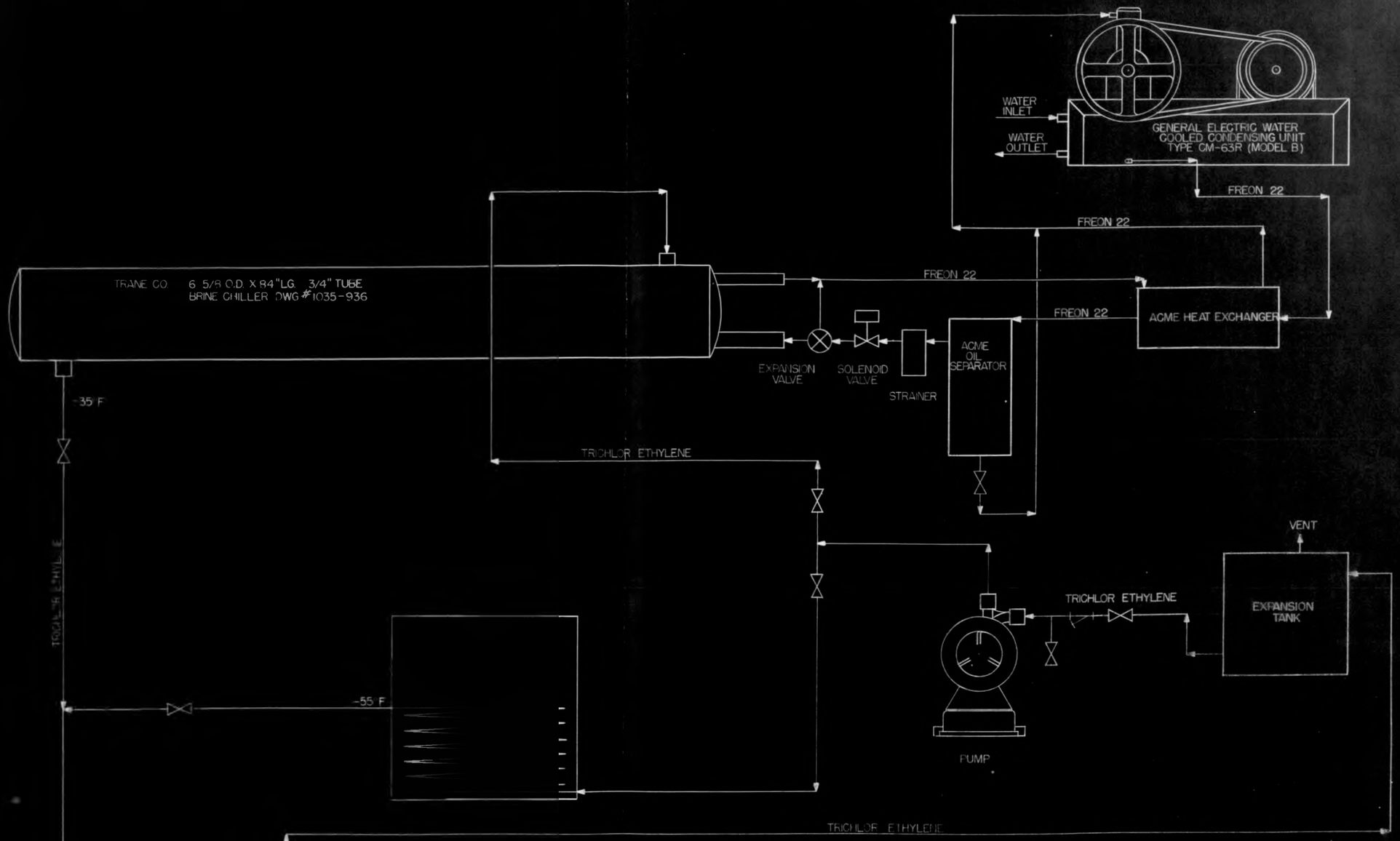


Photo #2



NOTE: FOR LOCATION OF EQUIPMENT SEE DWG.# 350-19-0

REVISION	REFER. DWG.
	343-19-0
	350-19-0
	351-19-0
APPROVED	

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

LOW TEMPERATURE REFRIGERATION SYSTEM FLOW SHEET

31-232-64

DESIGN: M.S. DRAWN: wel

SCALE: NONE

DATE: 4/16/46

DWG.	JOB	REV.
349	19	0

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 2[illegible].
Problem No. 64.

31

QOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

Operational Procedure

Since all the materials involved in this process either are hygroscopic or react with water, it is essential that they should be exposed to the air for as short a period as possible and that the equipment used be kept dry and closed when not in use. The 890 is used as received, but the CaF_2 is dried at ca. 250°C. in an electrically heated oven for at least eight hours before use.

The first operation in starting up this unit is the cooling of the low temperature condenser and receiver. Then, before anything else is done, the blower system should be put into operation, and the explosion alarm for Monomer should be turned on.

When the low temperature condenser and receiver are cool enough (below -40°C.), the dried CaF_2 - preferably still at 50-60° to minimize moisture absorption - is weighed and poured into the mixer. A molar ratio CaF_2:890 of about 0.83:1 is used. (For weights used see Table VI) The cover is shut and clamped in place, on a sponge rubber gasket. The temperature of the doughmixer bowl is taken, and if it exceeds 45°C., the bowl is cooled by passing cold water through the jacket. Then the 890 is siphoned through the loading port in the cover. As soon as this is closed, mixing and heating with hot water at 85°-90°C. is started. At the same time a single cake of dry ice is placed in the cooling bath of dry ice brine chiller (Dwg. 349-19-0), and a dry ice cooled trap is connected to the Monomer receiver.

In one-half hour the mixer will have heated sufficiently to start the reaction, and Monomer will begin to condense, as can be seen in the sight glass. This occurs at a recorded temperature of

48-60°C. in the large mixer and 56-68°C. in the small one. The heating is then regulated so that a small but steady stream of Monomer is observed in the sight glass. Toward the end of the reaction, steam alone under 15-20 lbs. pressure is used to heat the mixer. The temperature rises slowly during this period and reaches a maximum of ca. 100-110°C. by the time all dripping has ceased. At this point 80-85% of the theoretical Monomer should have been collected.

Once the Monomer is condensing properly, the transfer tank (Dwg. 358-19-0, see Construction section, p.822) should be attached to the receiver and cooled with dry ice. If desired, a Monomer sample for analysis may be withdrawn from the receiver into a cold test tube before the transfer tank is attached. In the case of the large doughmixer, within one-half hour of the start of condensation the receiver should be drained into this tank since the receiver is not large enough to hold all the Monomer produced. The drain line is left open and the transfer tank kept cool until condensation has ceased. In the case of the small doughmixer, the receiver need only be drained after the condensation has ceased. When the receiver has been drained, the transfer tank is detached, the Monomer weighed, the tank connected to a discharge pipe, and the Monomer allowed to boil away. This discharge pipe (protected against a possible flash-back) leads the Monomer directly to the exit of the blower system; hence the gas is rapidly dispersed, and there is no danger of building up explosive concentrations of Monomer and air.

The cooling system is then turned off and allowed to warm up. A slow stream of N_2 (about 1.5 cu. ft. per min.) is passed through the system. The dry ice-cooled trap should be weighed and emptied at least

QOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

every hour. When these weighings indicate no Monomer (15 g. or less) has been trapped in the last hour, the heat on the mixer is turned off and the exit line is clamped shut.

The mixer should be unloaded immediately, and the contents weighed and transferred to the kettles or storage cans as rapidly as possible. During this operation care must be taken to keep the Complex from coming in contact with the skin. The Complex is mainly in the form of a fine, gray-white powder, but some of it is caked on the blades and walls of the mixer. The free-flowing powder is first poured out by tilting the mixer bowl, then the cake is scraped from the walls and blades, the cover clamped on and the cake ground to an acceptable size. The doughmixer is again unloaded, and the contents weighed and added to the rest of the batch. The mixer should be closed again as soon as possible.

The liquid condensed in the 18°C. condenser is drained from the bottom of the trap. This is mainly 890 and is stored in a Monel receiver until the 891 is recovered from it. After 8 to 10 runs, or sooner if it appears necessary, the top of the trap is removed, and the collected powder taken out. This, together with material scraped from the lines, is charged to the doughmixer in a later run.

Table VII

Time Requirements

Operation	Large Mixer	Small Mixer
Cooling condensers	0.5 hr.	0.5 hr.
Loading mixer	0.25	0.25
Heating to 50°C.	0.5	0.5
Heating from 50°C. to first condensation	0.25-0.5	0.25-0.5
Period of condensation	4-5	2-3
Draining receiver	0.25	0.25
N_2 blow	5-6	4-5
Total	10.75-13 hrs.	7.75-10 hrs.

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

PAGE 557 eng-91

Variables and Variations

1. The CaF_2:890 molar ratio of 0.83 to 1 is chosen from the possible ratios because it results in a smaller charge of Complex to Step 2. As long as the charge in Step 2 does not stir well, the smaller the charge the more even is the heat distribution with a corresponding decrease in 891 loss in the CaF_2 residue (Ref. 475). In addition, there is naturally a large saving of CaF_2.

2. The heating and mixing are started as soon as possible after the addition of the 890, since it has been found that if the mixture is allowed to stand for a protracted time at room temperature there is an increase in the time necessary for reaction after heating is started.

3. The control of the reaction rate is necessary to prevent the flow of Monomer becoming so rapid that an undue amount of 890 and powder is carried along with it as entrained material.

4. Transfer of the Complex from the doughmixer to the kettles for Step 2 while hot lessens moisture pick-up and has been found to lower the loss in the second step in the form of trap liquid.

5. The origin of the CaF_2 gives rise to considerable differences in the time of reaction, properties of the Complex produced, the amount of recovered 890, etc. (Ref. 473, 445).

GOF 3692A PTD. IN U. S. A.

Step 2

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

Step 2

Chemistry

When the Complex produced in Step 1 is heated, it decomposes to give Tribnol and CaF_2.

$$\text{Complex} \xrightarrow{\text{Heat}} CaF_2 + \text{Tribnol}$$

This decomposition starts at approximately 250°, and after heating to 500°C., the residue is found to contain no 891. Since the reaction is endothermic, its rate is quite easily controlled by regulating the heat input.

A liquid side-product distills from the reaction vessel before and during initial stages of the main decomposition reaction. This liquid contains, on the average, 11.2% 891 and is thought to be mainly $BF_2(OH)H_2O$, which indicates that its formation is due to water, either present in the original CaF_2 or adsorbed by the Complex. (S.A.M. Report A-2121, p. 63).

Table VIII

Properties of Material

Material	State in Which Encountered	Molecular Wt.	Apparent Density g./cc.	Remarks
Complex	Powder	-	ca. 0.7	Burns on contact with skin.
Tribnol	Gas	67.82	$0.003^{20°}$	Irritating and toxic.
Residue CaF_2	Powder	78.08	ca. 0.8	Burns on contact with skin.
Trap Liquid	Viscous liquid	-	ca. 1.6	Corrosive; burns skin badly; irritating fumes.

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

Table IX

Usage Figures

	Large Kettle
Wt. Complex[1] lbs.	60
Approx. Vol., gals.	11.5
Tribnol (Theoretical wt., lbs.	30.6
Tribnol (% Yield	90
Trap Liquid, lbs.	1.2-1.5
Residue, lbs.	30

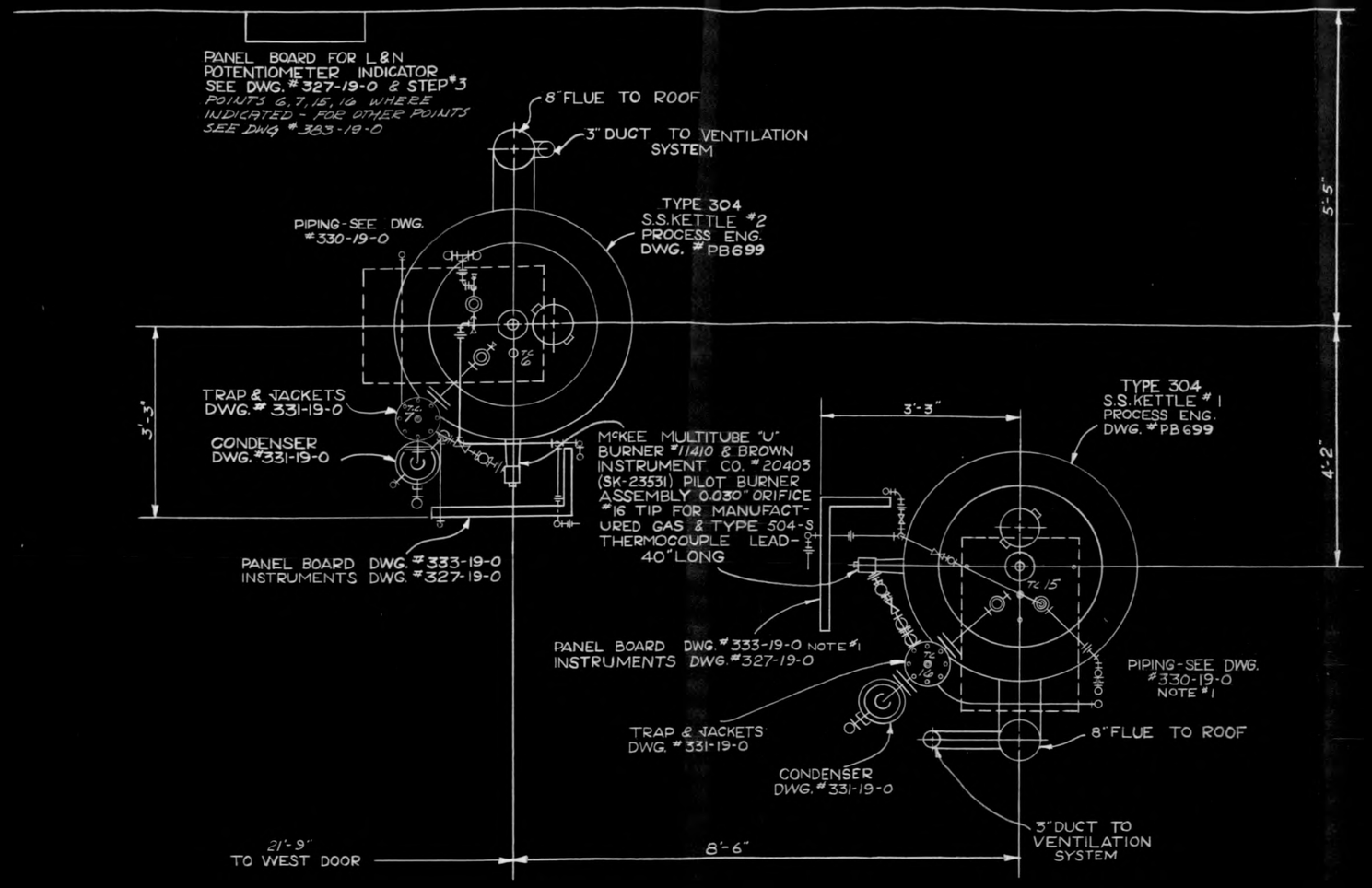
1. CaF_2:890 = 0.83:1.

Equipment

The equipment used in converting Complex to Tribnol is located in the center room of the building. (See Dwg 290-A-A, p.545). It consists of two units which are identical except for minor differences. Flow Sheet #2 shows one of these units.

The Tribnol evolved in the stirred kettle passes through a heated line into a heated powder trap filled with stainless steel wool, then into a water-cooled trap, where the liquid by-product is condensed and collected, and finally into the manifolds preceding the columns of Step 3. The CaF_2 residue is discharged through the pipe in the bottom of the kettle.

Originally the kettle, traps, and all the process lines up to the manifold were constructed of stainless steel. The corrosion, however, was so bad at some points - notably the top of the kettle, the lines to the heated trap and the heated trap and its thermocouple - that the lines and trap were replaced with Inconel. For future use it would be advisable to have the kettle as well constructed of Inconel.



	327-19-0
	330-19-0
	331-19-0
	333-19-0
	334-19-0
APPROVED	

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

LAYOUT — STEP NO. 2

31-232-64

DESIGN: M.S. DRAWN: WC

SCALE: 3/4" = 1'

DATE: 12-27-45

328 | 19 | 0

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

39

COMPLEX 61# FROM STEP #1

AIR 5# TO 10# P.S.I. GA. FOR BLOWING 5 HRS.

POWDER TRAP HEATED TO 200°C.

S.S. WOOL INSIDE

TRIBNOL + TAR

KETTLE
PROCESS @ 180°-250° FOR 10 HRS.
8-10 LBS./SQ. IN.

HEAT UP → 180°C. 1 HR.
BLOW AT 250°-350°C. 3 HR.
BLOW COOLING HEAT OFF 2 HRS.

TO STEP #3 ← TRIBNOL

WATER

WATER COOLED TRAP

GAS

BURNER

30# SOLID RESIDUE TO WASTE

WATER

APPROX. 1½# TAR

UNLOADING CAN

RECEIVER

30# SOLID RESIDUE TO WASTE

TAR RECOVERY TO SALT RECOVERY

REVISION	REFER. DWG.
	384-19-0
	343-19-0
	344-19-0
	385-19-0
APPROVED	

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

FLOW SHEET #2

31-232-64

DESIGN: M.S. DRAWN: wel

SCALE: NO SCALE

DATE: 2-6-46

DWG.	JOB	REV.
334	19	O

36.40

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

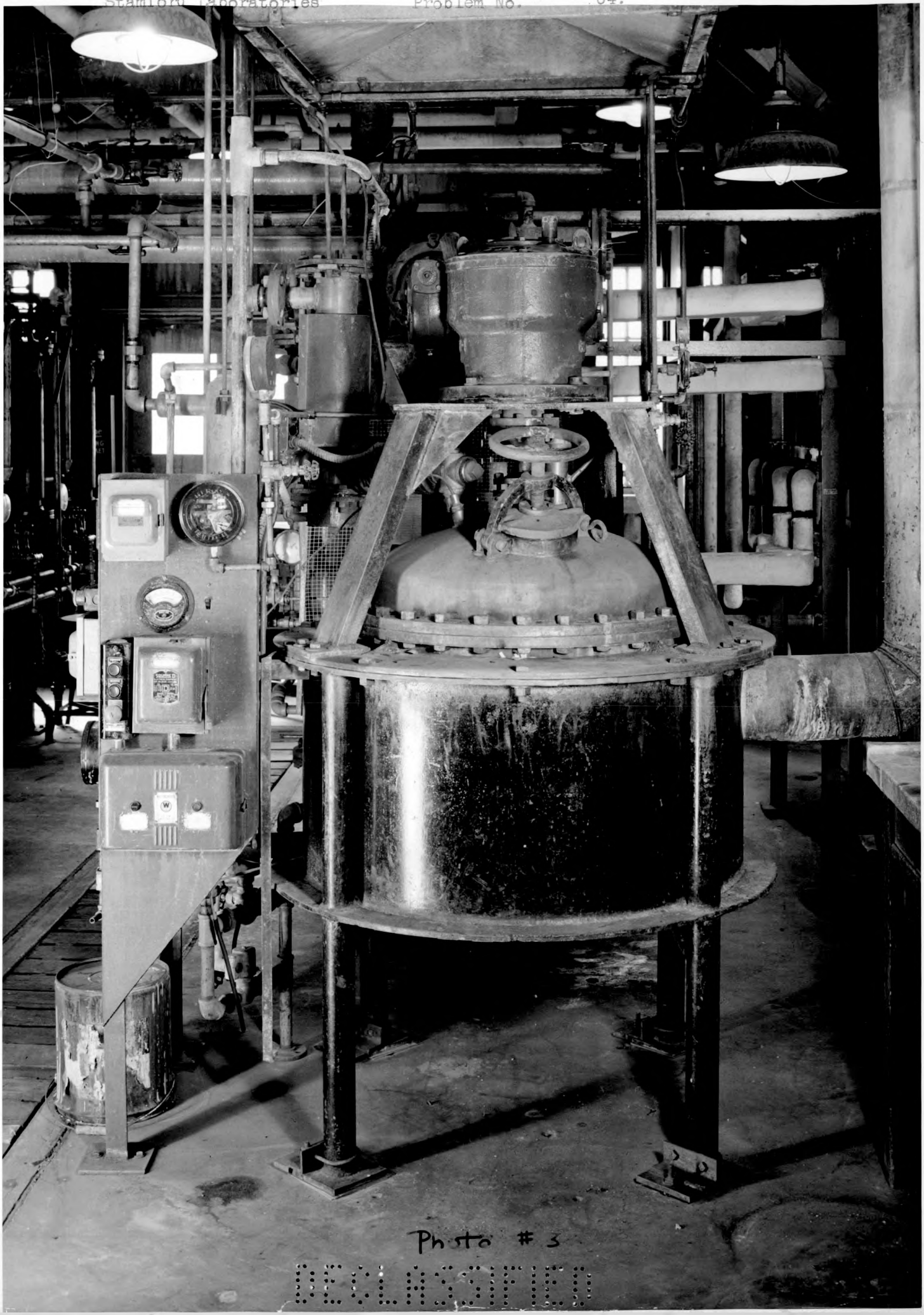
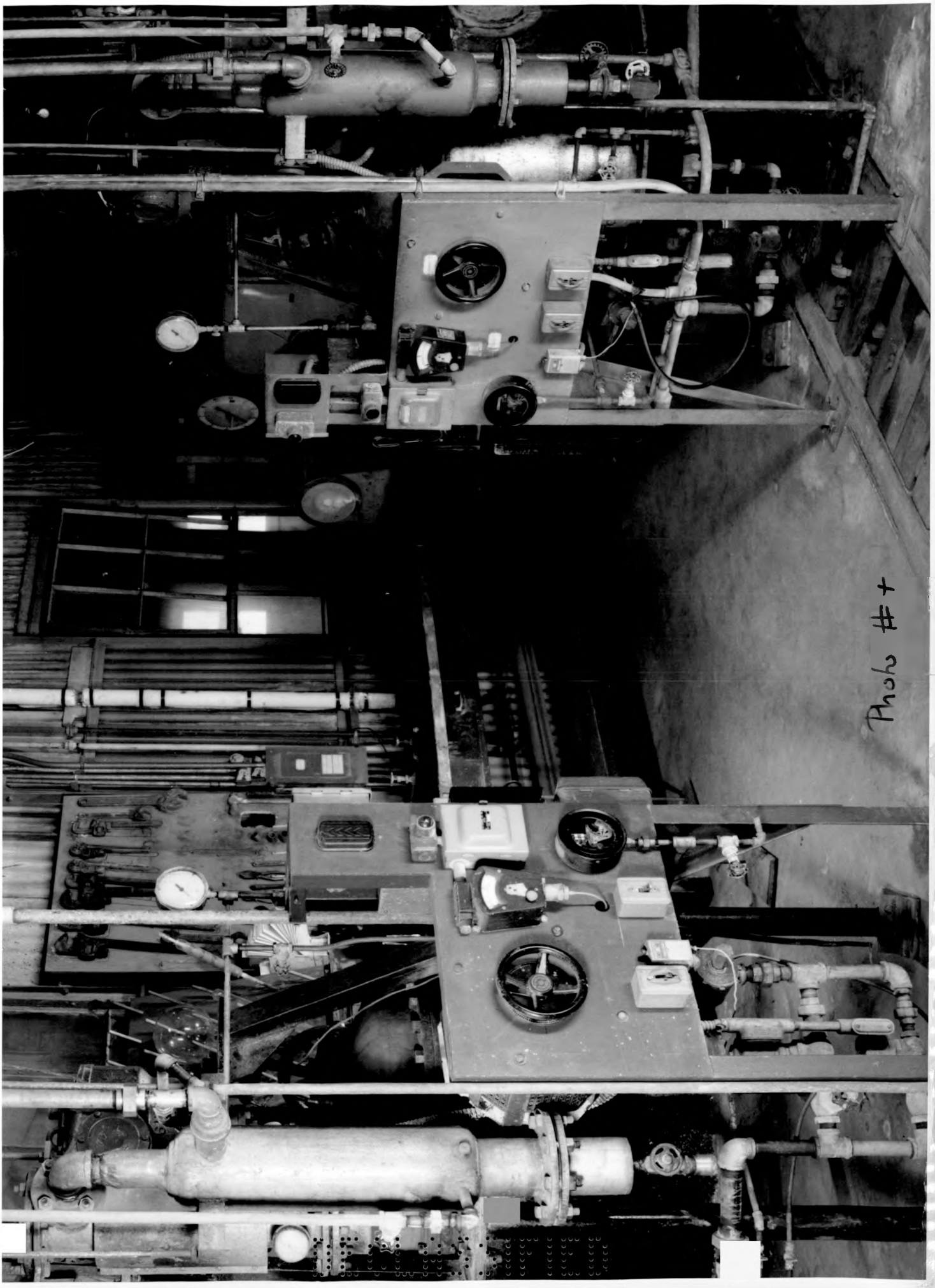
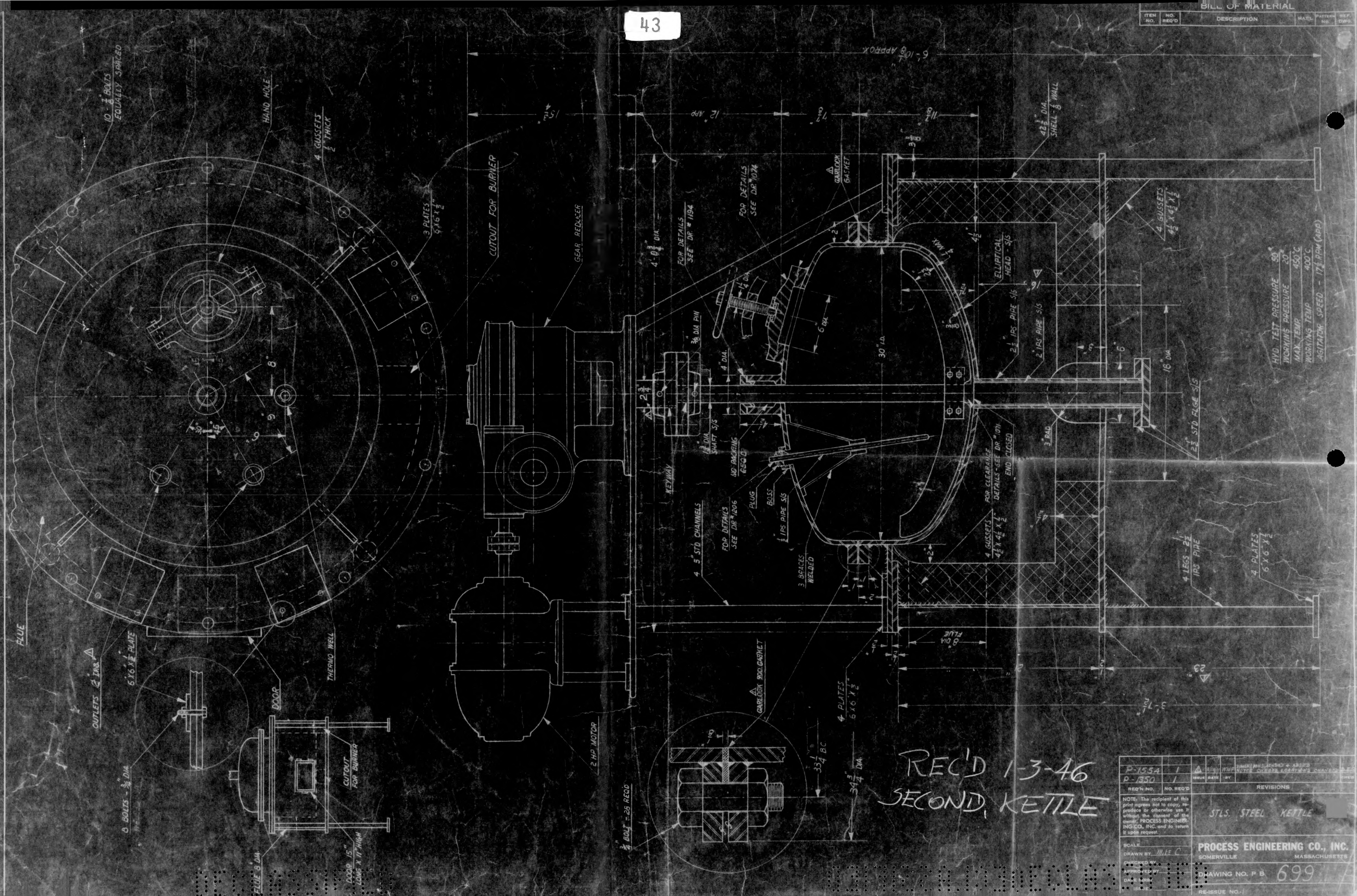


Photo #3



Prob #1

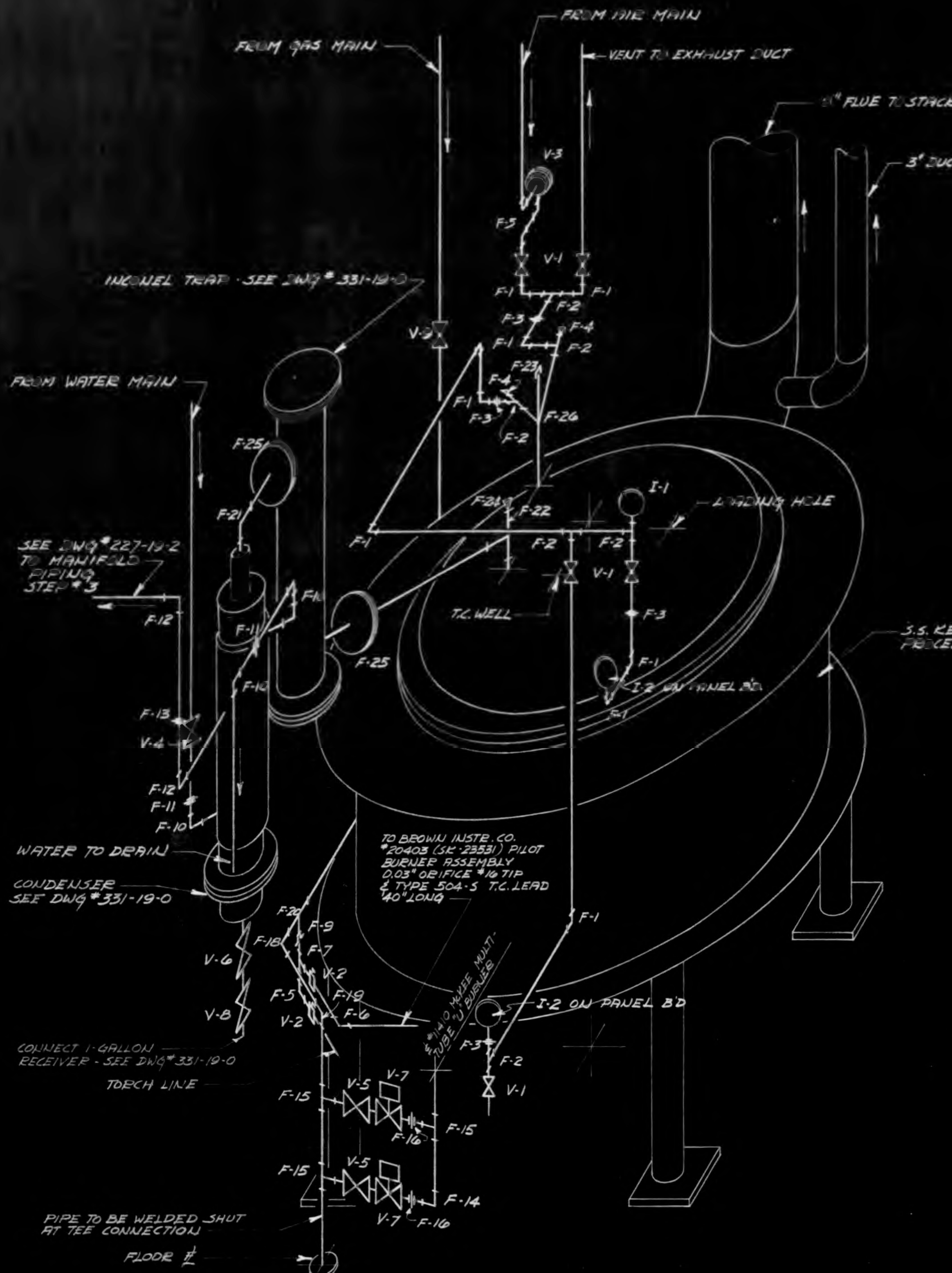
BINDING EDGE: 362 - 43

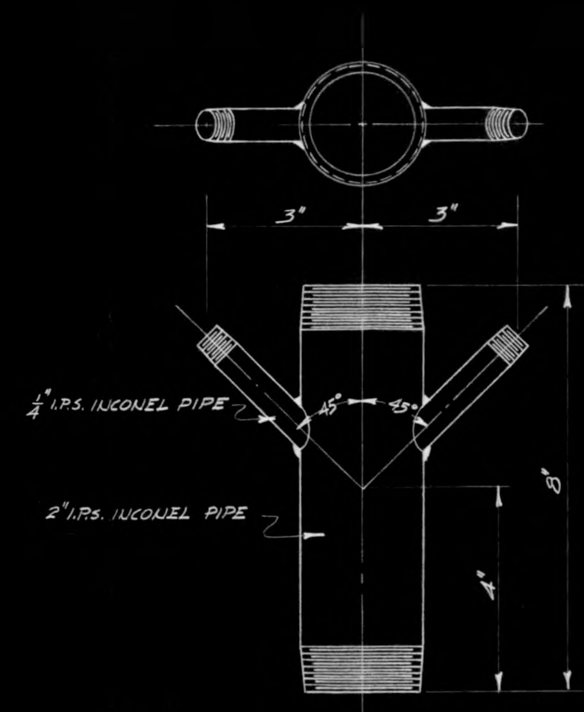


AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

DECLASSIFIED





DETAIL F-26
HALF SIZE

BILL OF MATERIALS

ITEM NO.	NO. REQ'D	DESCRIPTION	SIZE	MAT'L	NOTES
		FITTINGS			
F-1	9	90° ELL	1/4"	S.S.	SCREWED ENDS
F-2	6	TEE			
F-3	4	G.J. UNION			
F-4	2	PLUG			
F-5	6	90° ELL		BLK IRON	
F-6	1	45° ELL			
F-7	1	TEE			
F-8	1	G.J. UNION			
F-9	1	BUSHING	1/2" × 1/4"		
F-10	4	90° ELL	1/2"		
F-11	2	G.J. UNION			
F-12	2	90° ELL	1"	S.S.	
F-13	1	G.J. UNION			
F-14	1	90° ELL		BLK IRON	
F-15	3	TEE			
F-16	2	G.J. UNION			
F-17	1	90° ELL	1 1/4"		
F-18	1	45° STREET ELL			
F-19	1	90° ELL	1 1/4" × 1"		
F-20	1	TEE	1 1/4" × 1 1/4" × 1/2"		
F-21	1	90° ELL	2"	S.S.	
F-22	1	TEE			
F-23	2	CAP			
F-24	1	PLUG			
F-25	4	FLANGE		ST'L	INCONEL FACE
F-26	1	MANIFOLD	2" × 1/4"	INCONEL	SEE DETAIL (THIS DWG.)
		VALVES			
V-1	5	GLOBE	1/4"	BRONZE	
V-2	2	STOP COCK			
V-3	1	LINE REGULATOR			[illegible] # 40 0-50#
V-4	1	GLOBE	1/2"		
V-5	2	GLOBE	1"		WITH INDICATOR & THE TIMING UNIT
V-6	1	GATE		IRON BR'Z TRIM	
V-7	2	SOLENOID		BRONZE	AUTOMATIC SWITCH [illegible] TYPE [illegible]
V-8	1	BARSTOCK		S.S.	
V-9	1	GATE	1 1/2	BRONZE	
		INSTRUMENTS			
I-1	1	PRESS. GA. 0-60#	1/4"		
I-2	2	PRESS. CONTROL			MERCOID TYPE DA-231 RANGE 4 0-35#

NOTE:
1. PIPING FOR KETTLE NO. 1 TO BE SIMILAR BUT TO OPPOSITE HAND
2. WHERE STAINLESS STEEL (18-8) IS SPECIFIED, INCONEL IS PREFERRED

REV.	REF. DWG.	
	327-19-0	AMERICAN CYANAMID COMPANY DEVELOPMENT ENGINEERING DIVISION STAMFORD, CONN.
	328-19-0	
	331-19-0	PIPING FOR KETTLE No. 2
	333-19-0	
	334-19-0	

APPROVED

31-232-64
DESIGN: M.S.
DRAWN: M.S.
SCALE: 1 1/2" = 1'
DATE: 1-9-46

DWG.	JOB	REV.
330	19	0

362

49

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 28..
Problem No. 64.

GOF 3692A PTD. IN U. S. A.

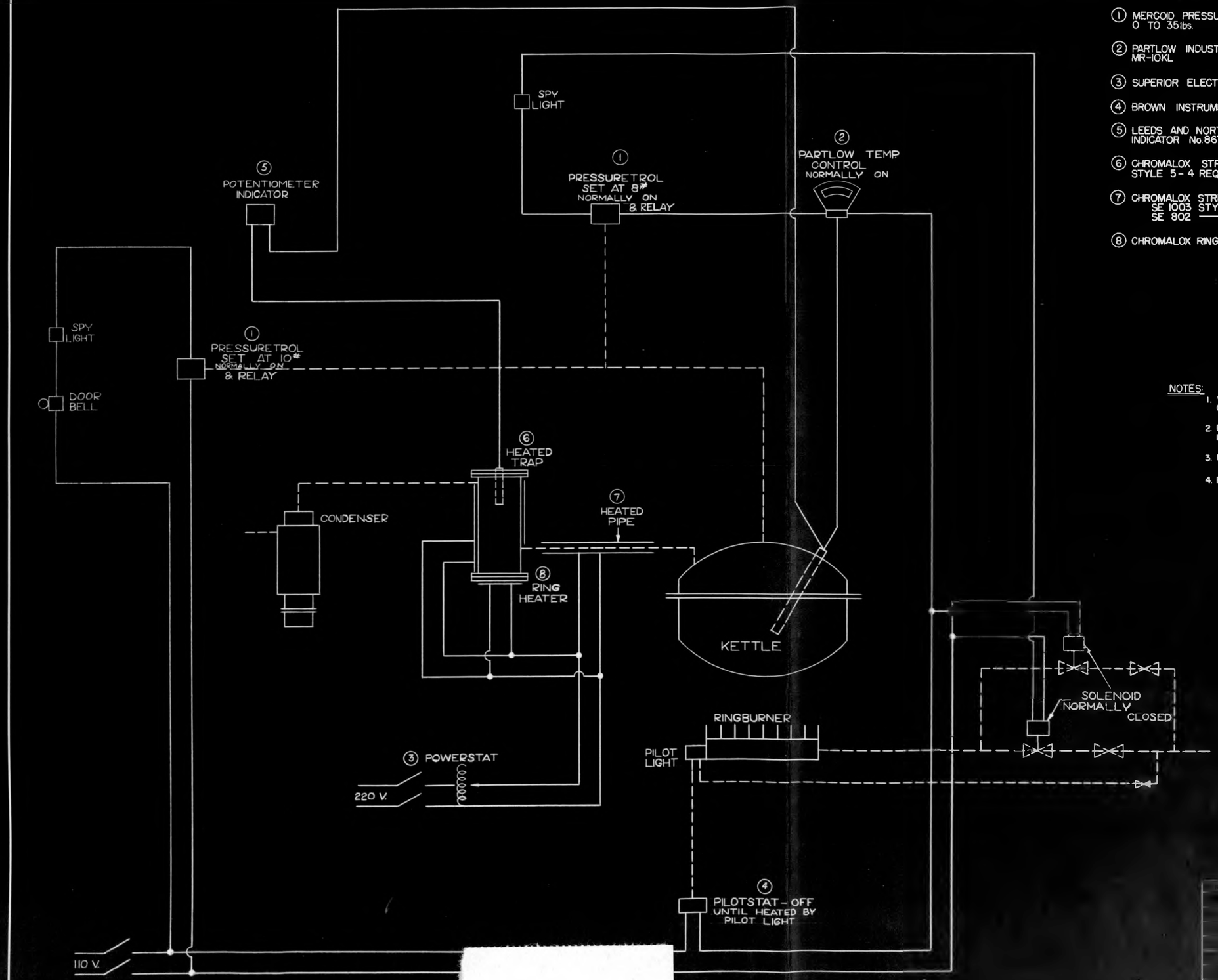
The stirred kettles are gas heated, and the electrically driven agitators move at about 18 rpm. Each kettle has one ring burner fed by two inlets, both of which are controlled by solenoid valves in addition to hand regulating valves. A pilotstat controls both solenoids. In addition one solenoid is opened and shut by a Mercoid "Pressurtrol" and a Partlow Temperature Control activated by the pressure and temperature in the kettle. A second Mercoid "Pressurtrol" operates a warning buzzer in case excessive pressures are built up in the kettle. The stirring motor controls, the pilotstat, and the automatic pressure and temperature controls are all mounted on a panel board beside the kettle (see Photo. #4, p.563). The lines to the first traps and the traps themselves are heated electrically with strip heaters. A Powerstat controlling these heaters is also located on each panel board.

The temperatures are read on an 18 point Leeds and Northrup Indicating Potentiometer located on a panel at the north side of the room.

The connections between the kettles, manifolds, and columns are such that a variety of operating combinations are possible. Normal procedure is for one kettle to be connected through a manifold to two series of columns. With the two steps thus connected, the reaction in the columns becomes a controlling factor in the operation of the kettles. Therefore the instructions for Step 3 should be used in conjunction with those below.

Operational Procedure

At least one-half hour before the kettle is to be charged the trap and line heaters should be turned on with the powerstat set at



INSTRUMENT LIST

① MERCOID PRESSURE CONTROL TYPE DA-231 RANGE 4 0 TO 35 lbs.

② PARTLOW INDUSTRIAL TEMPERATURE CONTROL MODEL MR-10KL

③ SUPERIOR ELECTRIC CO. POWERSTAT TYPE 1256 7.5KVA

④ BROWN INSTRUMENT CO. PILOTSTAT TYPE C418A1

⑤ LEEDS AND NORTHRUP POTENTIOMETER 18 POINT INDICATOR No. 8672 0 TO 600°C.

⑥ CHROMALOX STRIP HEATERS CAT. No. SE 1505 STYLE 5-4 REQ. EACH TRAP

⑦ CHROMALOX STRIP HEATERS
SE 1003 STYLE 5-2 REQ. FOR KETTLE No. 1
SE 802 ——— 2 REQ. FOR KETTLE No. 2

⑧ CHROMALOX RING HEATER A-30-1 REQ. EACH TRAP

NOTES:
1. WIRING DIAGRAM SHOWN FOR ONLY ONE COMPLETE KETTLE INSTALLATION.
2. FOR ITEM ⑤ (ONLY ONE REQ. FOR TWO KETTES) SEE ALSO STEP No. 3
3. FOR LAYOUT OF EQUIPMENT SEE DWG. 328-19-0
4. FOR PIPING SEE DWG. 330-19-0

REVISION	REF.
	328-19-0
	330-19-0
	331-19-0
	333-19-0

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

WIRING DIAGRAM
STEP NO. 2

31-232-64

DESIGN: M. S. | DRAWN: wel
SCALE: NONE
DATE: 12-6-45

DWG. 327 | 19 | 0

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

46

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

50. This gives them time to heat the trap and line to the proper temperature (ca. 200°C.) before the gas flow starts. The powerstat is used to hold the trap temperature at about 200°C. throughout the run.

The kettle is charged through the load hole in the top, which is closed again as soon as possible. A recommended gasket is "Garlock 900" liberally coated with "Key Paste" - a pipe joint compound with a molasses base. After the kettle is charged but before it is heated, the process line from the kettle should be opened to the proper manifold, while the latter should not be opened to the $AlCl_3$ columns until the pressure on the kettle side is equal to that built up in the columns by preheating (Dwg. 330-19-0, p.565).

The kettle is at first heated rapidly, with stirring, up to a temperature of about 150°C., the only precaution being that after the kettle and columns have been connected the rate of heating should not be great enough to produce in any one series of columns a flow equal to more than 20 mm. of CCl_4 on a "standard" flowmeter ("Standard" = 70 mm. Nujol ≡ 3 ft.^{3}/min. ≡ 0.85 lb. Tribnol per hr.) or to produce a pressure exceeding 12 lbs. The decomposition starts at a recorded temperature of ca. 190°C. This temperature should be approached slowly as it is subject to some variation with the weight of the charge and the previous rate of heating. This is because the recorded temperatures are not the true temperatures of the charge since the thermocouple well is not usually in the charge.

Once the decomposition has started, as evidenced by the increase in flow and pressure, the reaction rate is controlled by the heat input so as to give the required flow to the columns. This is done by setting the automatic gas controls to hold the pressure at 2-3 lbs.

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

above the back pressure of the columns and regulating the flow into the columns by needle valves. In order to obtain constant pressure and flow, the gas inlet which is not regulated by the "Pressurtrol" should be opened far enough to almost keep the pressure up in the kettle. Then the regulated valve is opened just a little (see Dwg. 327-19-O, p.567). When the kettles are regulated in this manner the temperature remains between 180° and 210°C. until most of the Tribnol in charge of Complex has been liberated and the pressures and flow begin to drop.

At this point the temperature begins to rise. The heating should be increased so that over a period of 1.5 hours the temperature is raised to ca . 350°C. (See below under "Variables and Variations".) The stirrer should be reversed several times after the temperature has risen about 20° in order to jar loose any unreacted Complex cake which may be stuck to the kettle walls and to mix thoroughly and react uniformly the kettle charge (see below under "Variables and Variations", Note 2). If this causes a sudden increase in flow and pressure, the stirrer should be frequently reversed until there is no longer any flow. Care should be taken that the bottom of the kettle does not become too hot even if the recorded temperature is still low due to poor heat exchange.

As soon as the flow has almost ceased and the pressure in the kettle has dropped, the tar collected in the cooled trap should be drained into a Monel receiver (see "Auxiliary Equipment, Step #2" - Construction section) and stored for recovery work. A slow stream of air, dried by being passed through a Pittsburgh Lectrodryer, is now passed through the kettle and column set-up providing the temperature has risen to at least 245°C. (It will be almost 290°C. if heated up properly.) The air is regulated so that the total flow of air and

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

PAGE 570eng-91

Tribnol through each column series is about 15 mm. on a "standard CCl_4" flowmeter. After blowing the kettle hot (245°-350°C.) for 3 hours, the heat is turned off, and the pot allowed to cool - the air flow being continued for 2 more hours. The temperature will now be about 150°C. The air is shut off, the stirring is stopped, and all the process valves from the kettle to the columns are closed.

The kettle should be discharged as soon as possible. This is done through the hole in the bottom of the kettle. Part of the Residue will flow out as a powder when the agitator is moved. The rest, which is caked on the walls of the kettle, should be scraped out reasonably thoroughly. A sample of the residue is analyzed for 891 and the rest is stored (see "By-Products" above in Table IV).

The kettle should be closed up again as soon as possible. However, before this is done the gaskets which were removed in discharging the kettle should be inspected and replaced, if necessary. The line leading from the kettle to the heated trap should also be checked to make certain that it is not plugged at the exit from the kettle. Then the stuffing box should be inspected to see if it needs additional packing.

The cooled trap should be drained again before the next run is started, and the heated trap should be inspected and cleaned every 8-10 runs.

Table X

Time Requirements

Operation	
Loading	0.25 hr.
Heating to 150°C.	1
Heating from 150°C. to reaction temperature	1[2]
At reaction temperature[1]	8[2]
Heating to 290°C.	1.5
At 290-350°C.	3
Cooling	2
Unloading	1
Total	17.75[3] hrs.

1. When using two series of columns at 80 mm. (CCl_4) flow.
2. For Complex from 5 gals. of 890.
3. To this must be added about 3-1/2 hrs. to blow, unload, and load $AlCl_3$ columns before a new run can be started using the same column series.

Variables and Variations

1. The flow rates during the reaction and purging with air are governed by conditions existing in the $AlCl_3$ columns and the explanation of these rates will be found in that section dealing with Step 3.

2. The 350°C. limit for the heating of the kettles is to prevent damage to the kettle through overheating. This limit, however, varies widely with the batch of CaF_2 used - and, of course, depends on the kettle in operation. Some batches of General Chemical CaF_2 gave Complex which could not be heated to 350°C. even though the bottom of the kettle was almost a white-red - which is much too hot. Others heated up very readily. Complex prepared from Harshaw CaF_2 heated so readily to over 400°C. that the bottom of the kettle was only a very dull red. These results are a direct consequence of the stirring qualities of the Complex (Ref. 444-446, 474). The Residue

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

PAGE 57leng-91

contains about 0.17% 891 when heated to 350°C. and 0.12-0.02 when heated to 410-450°C.

3. Probably 2 hours of air blow after the heat has been turned off the kettle are sufficient to purge the kettle, but since the columns must be purged for an additional length of time and since continuing the blow through the kettle may speed the cooling, the air flow is continued through the kettle until it is cool enough to discharge.

4. The cooled trap is drained before the purging is commenced, since the trap liquid contains Tribnol which might be given off, thus hindering the purging of the rest of the system.

5. Letting the residue stand for several days before discharging the kettle probably does little harm. However, discharging the kettle while warm should reduce to some extent the moisture picked up by the kettle and is also to be recommended because the caked residue may be removed more easily warm than cold.

6. As far as is known the reaction may be stopped for a short period of time and then started again without appreciable loss in yield provided the kettle is not opened. It seems advisable in such a case to keep the heat on the kettle, controlling it by the automatic controls.

7. Any reopening of the kettle once the reaction has started - to replace a gasket, for example - will obviously result in a loss in yield, if only because of loss of gaseous Tribnol.

8. If the stirring mechanism fails, either the reaction can be completed without stirring or the kettle may be discharged and the charge run in another kettle. If the reaction is nearly completed, continuation without stirring will result in a 1-5% loss, while if near

GOF 3692A PTD. IN U. S. A.

the start of the reaction, the loss may be as high as 10-12%. Running without stirring usually results in lower recorded temperatures due to poor heat exchange. The reaction takes much longer, and considerable care must be taken not to overheat the bottom of the kettle. Discharging and loading into another kettle leads to a loss of 5-10% in yield.

GOF 3692A PTD. IN U. S. A.

Step 3

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

PAGE 573eng-91

Step 3

Chemistry of Process

The reaction between Tribnol and $AlCl_3$ is a straightforward double decomposition reaction to give a gaseous product- Chlorthane, and a non-volatile product- AlF_3.

$$\text{Tribnol} + AlCl_3 \longrightarrow \text{Chlorthane} + AlF_3$$

With sufficient excess of $AlCl_3$, the conversion of Tribnol to Chlorthane is quantitative.

While the reaction will take place at a temperature as low as 50°C., it proceeds more readily at higher temperatures. 100°C. has been found to be a satisfactory starting temperature. Since the reaction is exothermic, this temperature will increase when the reaction begins. Heats of formation indicate an endothermic reaction, from which it has been concluded the heat of formation of aluminum fluoride is in error. The exothermic nature of the reaction also causes a "hot spot" when the reaction is run in a tube, and this facilitates following the course of the reaction.

When a charge of $AlCl_3$ becomes partially exhausted, increased activity may be obtained by heating the $AlCl_3$ to temperatures approaching the active sublimation point (178°C.). This regaining of reactivity is thought to be caused by the breaking up of particles of $AlCl_3$ which have become coated with AlF_3. (Ref. 16-28, 91-95, 130-137, 203-207; S.A.M. Report A-2122, pp. 1-19).

A low iron content in the $AlCl_3$ is desirable, since $FeCl_3$ may be volatilized, thereby contaminating the product. Likewise, any appreciable quantity of silicon is undesirable since $SiCl_4$ and Chlorthane

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

PAGE 574eng-91

form a liquid complex stable at room temperatures and some of the other silicon halides would contaminate the Chlorthane. The $AlCl_3$ particle size is very important. The material must be fine in order to obtain good reaction, but on the other hand if too fine, the resulting back pressure from passage of the gaseous Chlorthane through the finely divided $AlCl_3$ becomes too high. In addition the reaction rate increases greatly, so that it is difficult to keep the temperature below the sublimation point of the $AlCl_3$; hence the reaction columns plug very easily. Experience has shown that the specifications given below are satisfactory. (Ref. 18-19).

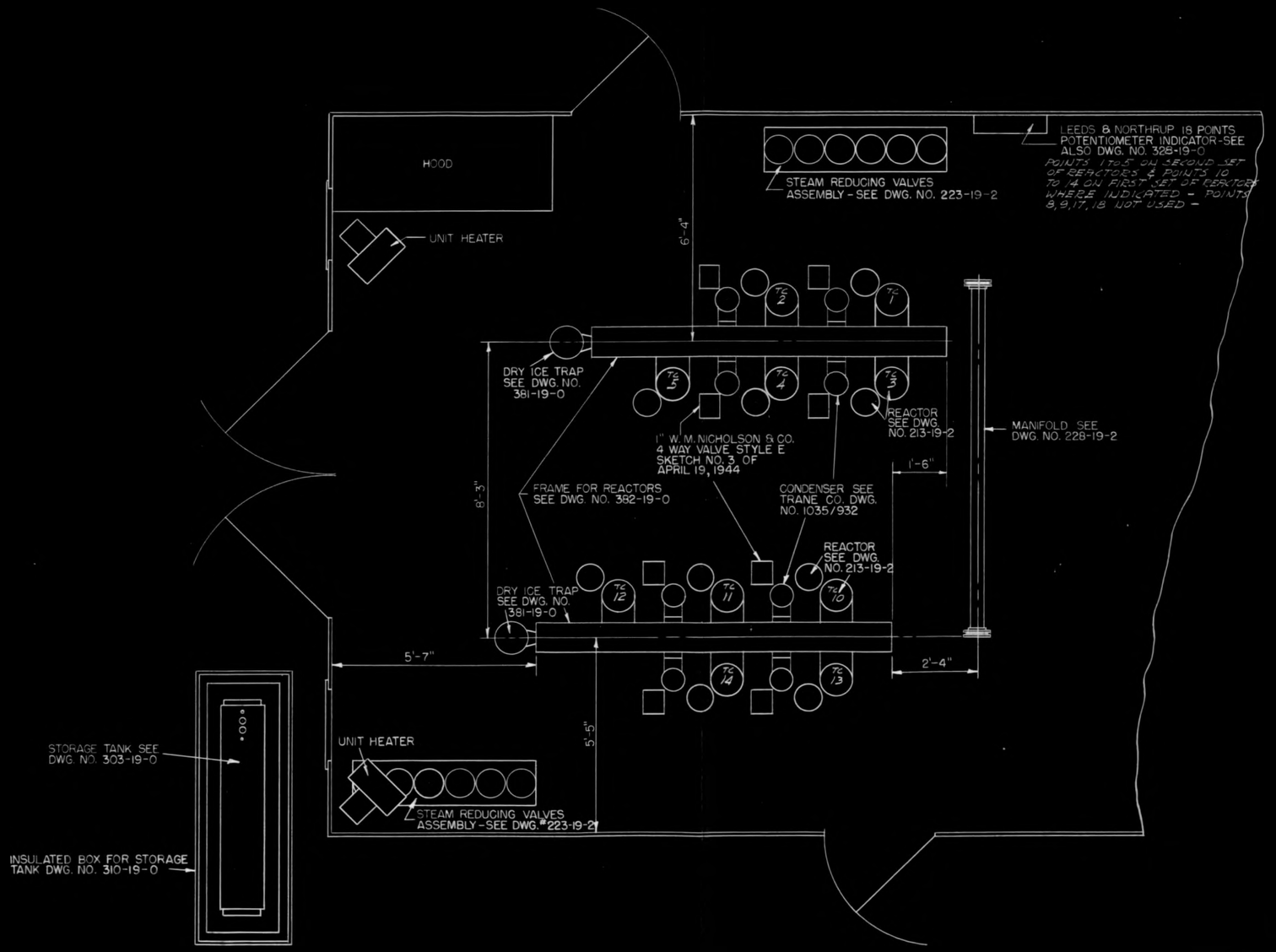
Table XI

Specifications for Aluminum Chloride

70% through	60 mesh
100% "	40 mesh
$FeCl_3$ =	0.1% or as Fe 0.04%
$AlCl_3$	99%
Non-volatiles	0.5-0.7%
$SiCl_4$	0.1% or less
$TiCl_4$	0.02-0.03%

Equipment

The equipment for the conversion of Tribnol to Chlorthane is located in the front part of the center room of the building. (See above, Dwg 290A-A, p.529 and Dwg. 383-19-0 which follows). The fundamental unit of the set-up consists of the vertical $AlCl_3$ column, a powder trap, a condenser and receiver. The column is 5 feet long, made of 5" diameter stainless steel pipe with flanged ends. The top and bottom halves are jacketed independently for steam at 0-140 psi. The Tribnol enters the bottom of the $AlCl_3$-filled column and the Chlorthane which is formed, plus any unconverted Tribnol, leaves at the top.



NOTE:
FOR MANIFOLD PIPING SEE DWG. NO. 227-19-2
" PROCESS " " " " 218-19-2
" STEAM " " " " 215-19-1
" WATER " " " " 379-19-0
" COOLANT " " " " 380-19-0
" DWG. OF RECEIVER " " " 381-19-0
" " " CRUDE STORAGE TANK SEE DWG. NO. 229-19-0

FOR EQUIPMENT SEE DWG. NOS. 223-19-2, 327-19-0, 213-19-2, 228-19-2, 382-19-2, 303-19-0, 310-19-0

FOR FLOW SHEET SEE DWG. NO. 344-19-0

SUPER. DWG.	
	SEE NOTE

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

FLOOR PLAN-STEP NO. 5

31-232-84

DESIGN: M.S.
SCALE: 1/2" = 1 FT.
DRAWN: [illegible]
DATE: JUNE 11, 1945
DWG. NO. 0
REV.

56

DECLASSIFIED

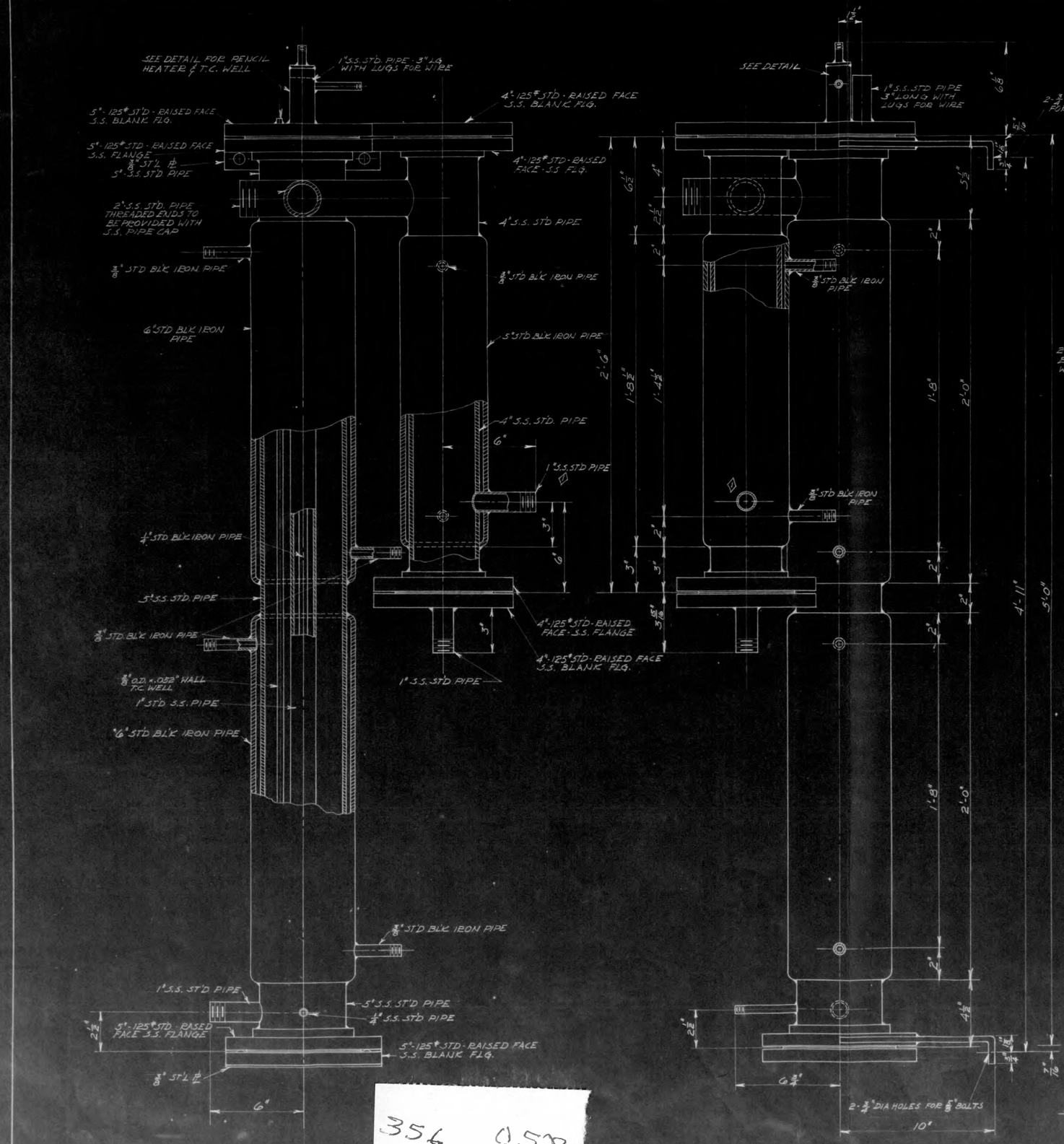
GOF 3692A PTD. IN U. S. A.

The $AlCl_3$ vaporized or entrained in the effluent gases is caught in the trap, which is water cooled and filled with glass wool. The trap removes $AlCl_3$ powder and vapor. The gases then enter a condenser with 2 sq. ft. of condensing surface cooled to 0°C. by a circulating glycol-water mixture. The Chlorthane is condensed and collected in a jacketed receiver held at 0°C., while the Tribnol and any uncondensed Chlorthane pass out the exit line of the receiver. (Dwg. 213-19-2).

To obtain complete conversion of Tribnol to Chlorthane while at the same time using the $AlCl_3$ as efficiently as possible, two of these units are used in series. As a further precaution against incomplete conversion of Tribnol two such series of two columns each have their exit gases led through a common third column, which is followed by a dry-ice trap instead of a condenser held at 0°C. The equipment available consists of two of these five column units.

The gas flow through the columns, as labeled in the flow sheet, may be in the order 1-2-5 and 3-4-5 or 2-1-5 and 4-3-5. The photograph of p.580 shows from left to right columns, 1,2,5 and the dry ice.trap. The former 1-2-5 arrangement is called "forward flow" and the latter "reverse flow". It is also possible to completely by-pass either column(s) 1(3) or 2(4) and its accessories should the need arise. A four-way valve at the top of each condenser permits by-passing of the condenser and receiver of any column.

The rate of Tribnol flow entering from the manifolds to the columns is controlled by needle valves (Flow sheet). "Normal flow" is 0.85 lb. Tribnol per hour (approximately 3 $ft.^3/min.$) and a "standard flowmeter" is one on which such a flow reads 70 mm. of Nujol. All flows are expressed in terms of these.



NOTE:
TEN COMPLETE UNITS REQUIRED
USE ⅛" HYCAR GASCETS AT FLANGED JOINTS

REF. DWG	REV.	
383-19-0, 218-19-2		
379-19-0,	REV. ⓑ	7-22-44
	REV. ⓒ	5-23-44

AMERICAN CYANAMID CO.
STAMFORD, CONN.

REACTOR
31-232-64

DESIGN: W. F. C.
SCALE: 3" = 1 FT.
DATE: MAY 13, 1944
DRAWN: M. S.

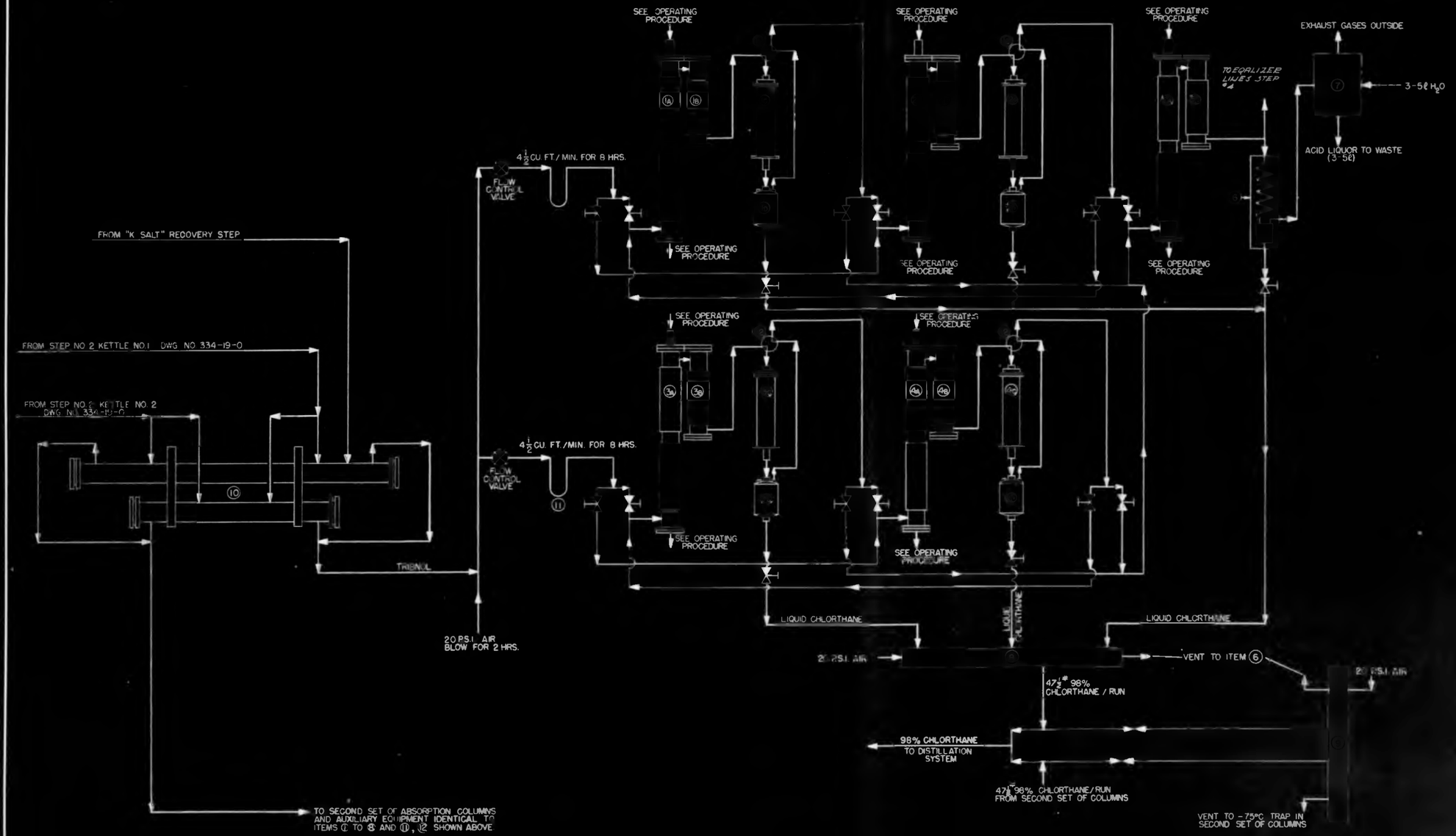
DWG.	JOB	REV.
213	19	2

FILE: 9-2

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

DECLASSIFIED



EQUIPMENT LIST

(1a)(2a)(3a)(4a)(5a) STEAM HEATED ABSORPTION COLUMNS AT 110°-200°C. FILLED WITH $AlCl_3$

(1b)(2b)(3b)(4b)(5b) WATER COOLED DUST TRAP @ 2°C.

(1c)(2c)(3c)(4c) CONDENSER at 0°C.

(1b)(2b)(3b)(4b) RECEIVER at 0°C.

⑥ TRAP at -75°C.

⑦ BUBBLE TANK

(8) 100# STORAGE TANK at 0°C.

(9) 200# STORAGE TANK at 0°C.

⑩ MANIFOLD

⑪ FLOW METER

⑫ FOUR WAY VALVE

OPERATING PROCEDURE

THE SYSTEM WILL BE OPERATED WITH FLOW THROUGH COLUMNS 1 TO 2 TO 5, 3 TO 4 TO 5 IN THE ORDER INDICATED, AND THROUGH COLUMNS 2 TO 1 TO 5, 4 TO 3 TO 5 IN THE ORDER INDICATED ALTERNATELY IN SUCCESSIVE RUNS. FOR FLOW 1 TO 2 TO 5, 3 TO 4 TO 5 VALVES INDICATED ⋈ WILL BE CLOSED AND VALVES INDICATED ⋈ WILL BE OPEN; FOR FLOW 2 TO 1 TO 5, 4 TO 3 TO 5 VALVES INDICATED ⋈ WILL BE OPEN AND VALVES INDICATED ⋈ WILL BE CLOSED; IN EACH CASE VALVES INDICATED ⋈ WILL BE CLOSED DURING ANY ONE RUN AND OPENED AT THE END OF THE RUN.

INITIALLY ALL COLUMNS ARE FILLED WITH $AlCl_3$. AFTER ONE RUN THROUGH 1 TO 2 TO 5, 3 TO 4 TO 5 APPROXIMATELY 25# OF SOLID RESIDUE WILL BE EXTRACTED FROM COLUMNS 1 AND 3 AND REPLACED WITH APPROXIMATELY 34# OF $AlCl_3$. AFTER THE NEXT RUN THROUGH 2 TO 1 TO 5, 4 TO 3 TO 5 SOLID RESIDUE WILL BE EXTRACTED FROM COLUMNS 2 AND 4 AND REPLACED WITH $AlCl_3$, COLUMN 5 WILL HAVE RESIDUE EXTRACTED AND IT WILL BE CHARGED WITH $AlCl_3$ WHEN 89% CONTENT OF ACID LIQUOR FROM ITEM ⑦ INCREASES.

REV.	REFER. DWG.
	383-19-0
	218-19-0
	227-19-0
	385-19-0
	404-19-0
	384-19-0

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

FLOW SHEET NO. 3

31-232-64

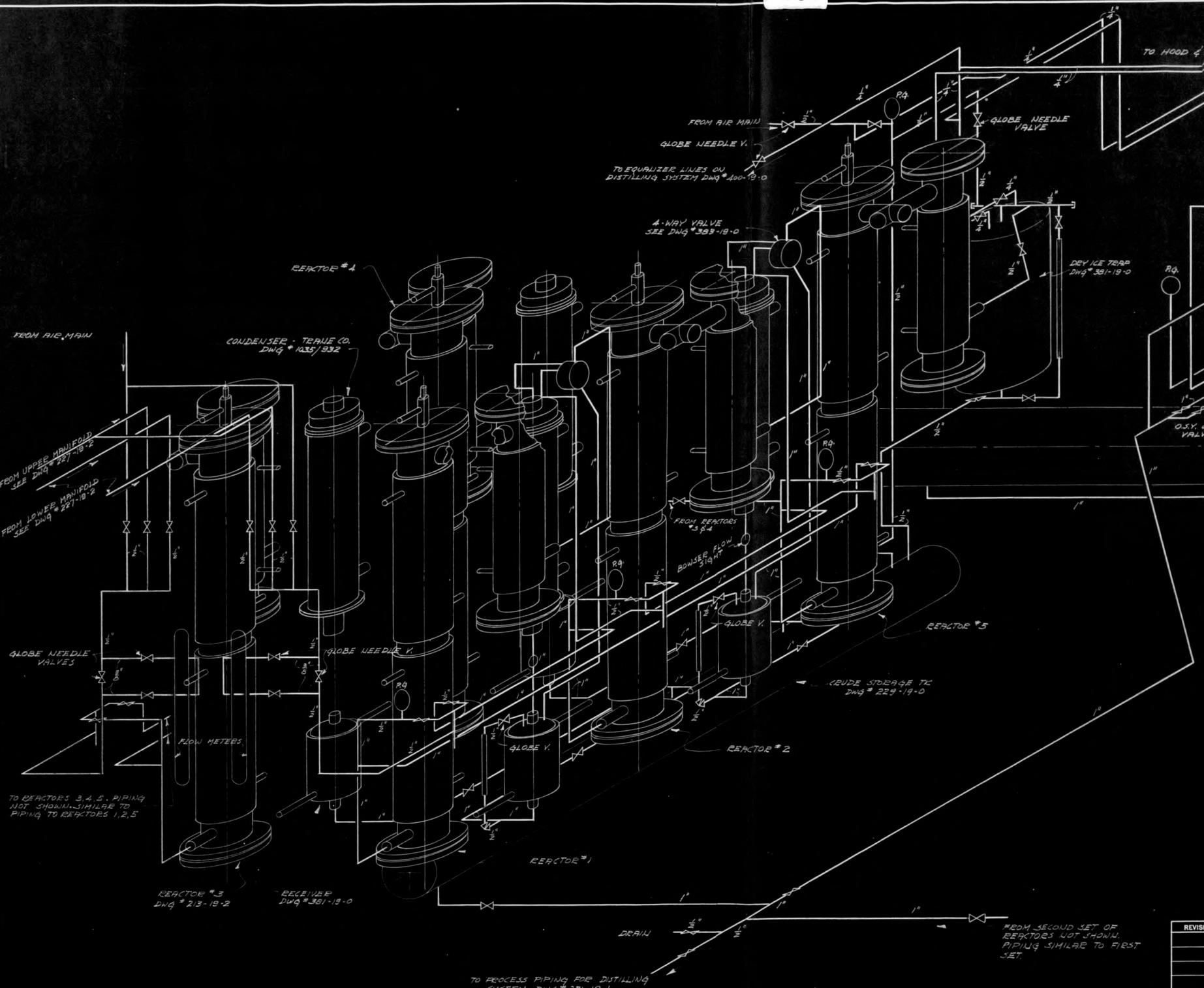
DESIGN: M.S.
SCALE: NONE
DATE: 5-7-46

DRAWN: wel

DWG.	JOB	REV.
344	19	0

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.



NOTE:
BLACK IRON I.P.S. PIPES & FITTINGS THROUGHOUT. IRON BODY, BRONZE TRIM GATE VALVES EXCEPT WHERE NOTED

REVISION	REFER. DWG.
	400-19-0
	383-19-0
	227-19-2
	213-19-2
	381-19-0
	229-19-0
	303-19-0
	231-19-1

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

PROCESS PIPING FOR REACTORS

31-232-64

DESIGN: M.S.	DRAWN: M.S.		
SCALE: NONE	DWG.	JOB	REV.
DATE: JUNE 18, 1946	218	19	2

60

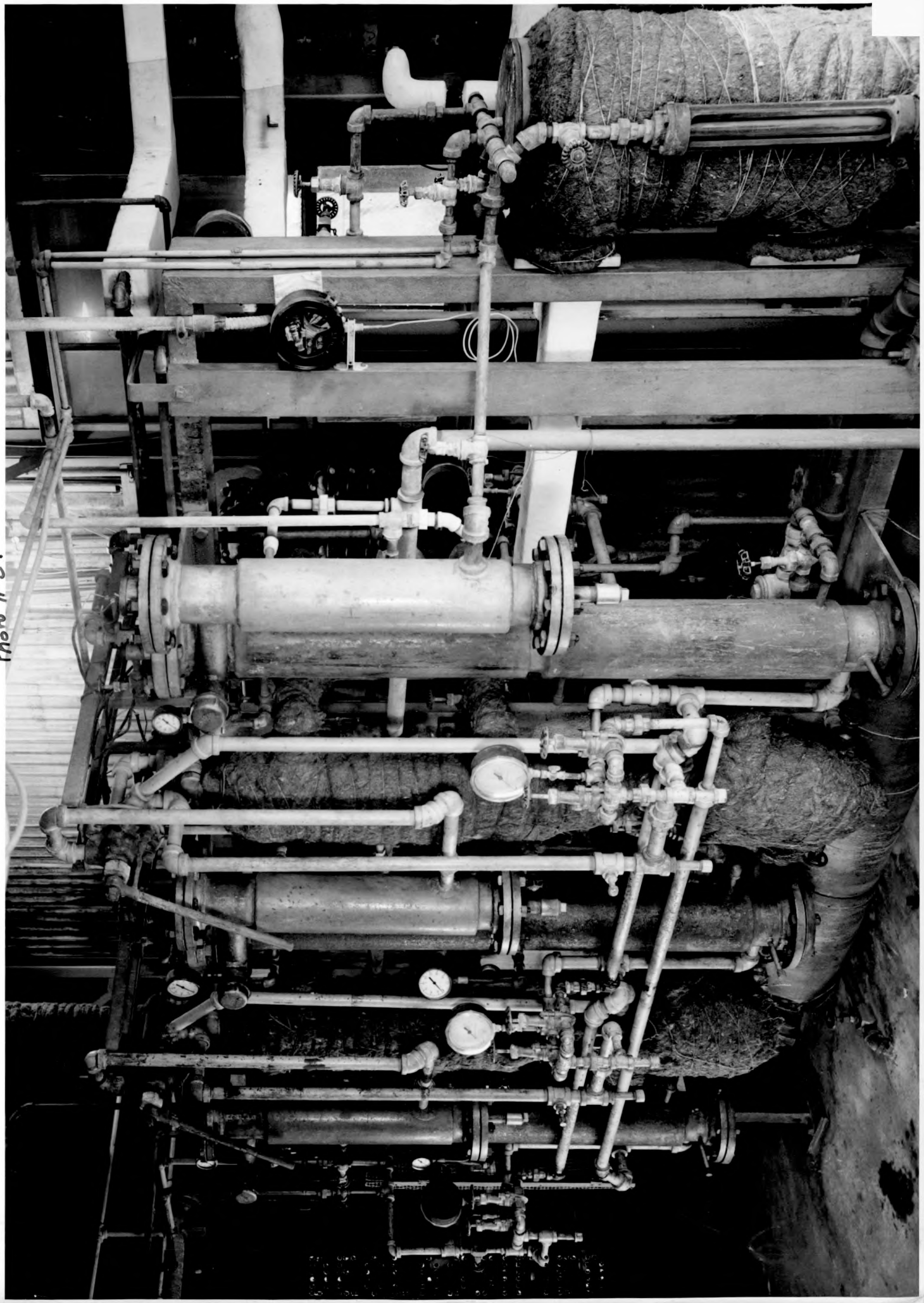


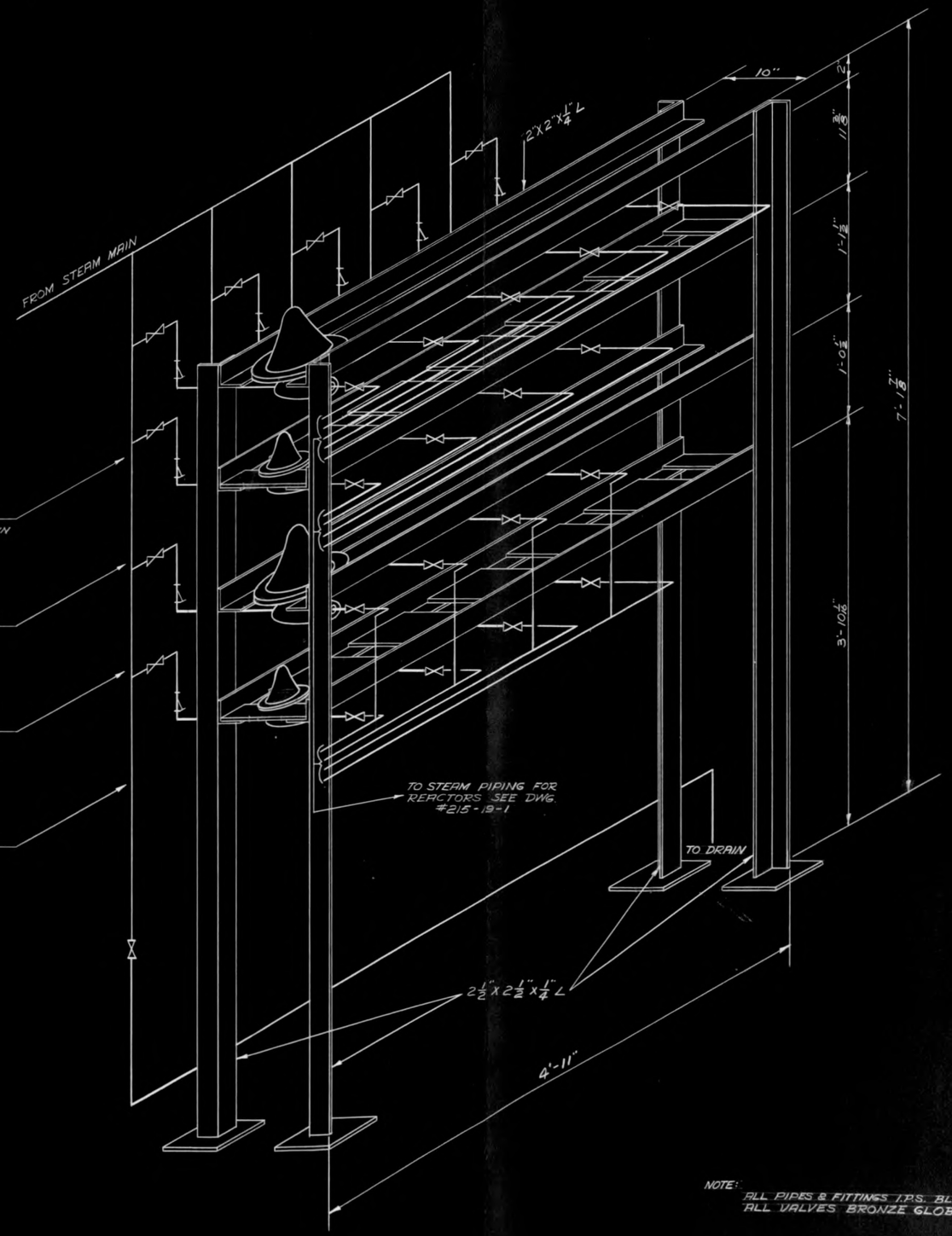
Photo #5.

3627461

There are two vent lines after the water-cooled powder trap of the third column, one leading through and one by-passing the dry ice trap. The former is normally used and exits through a water trap where the last traces of Chlorthane are absorbed. A simple yet satisfactory trap can be made by connecting four one-gallon bottles in series. The second and fourth are each filled with 3 l. of water, through which the gas is bubbled. The first and third are empty catch bottles to take care of suck-backs. A drying tube should be placed between the system and the first bottle.

The pressures throughout the system are read on the gauges indicated in the flow sheet (see p.578) - the large gauges shown in the photograph. Each column has a thermocouple well running throughout its length at its center. Movable thermocouples are used to read the temperatures at any levels in the columns. These temperatures are read on the Leeds and Northrup 18 point indicator mounted at the north side of the room.

In addition to two jackets, each of the columns in the series has a thimble located at the center of the column for steam heating. (See Dwg. 213-19-2, p.577). The steam pressure controls for each five column set-up are mounted on a frame separated from the column support. In addition to shut off valves, the steam pressure in each jacket of each column is controlled by an adjustable high pressure (30-140 lbs.) and an adjustable low pressure (0-40 lbs.) reducing valve. A by-pass around the steam trap in the exit line permits heating by steam "blow" to atmosphere. The thimbles may be turned on and off independently, but the pressure controls are those for the upper jacket. The "third" columns (Column 5 on flow sheet, p. 578) have only one jacket covering the whole column, which is regulated only by a low pressure steam valve.



NOTE:
ALL PIPES & FITTINGS I.P.S. BL'K IRON
ALL VALVES BRONZE GLOBE

REVISION	REFER. DWG.
	215-19-1
	383-19-0

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

REDUCING VALVES ASSEMBLY

31-232-64

DESIGN: M.S. DRAWN: wel

SCALE: NONE

DATE: JUNE 20, 1946

DWG.	JOB	REV.
223	19	2

30 63

63

The individual Chlorthane receivers following the condensers on the columns together with the dry ice traps drain into two main storage tanks, one for each five column set. Each of these tanks is connected to the weigh tank on the still and equipped with a dry air line and a vent line through the dry ice trap. They are also connected to an extra storage tank with twice the capacity and so constructed that it may be cooled directly with ice should the regular mechanical refrigeration system fail.

This refrigeration system cools the condensers, receivers, and storage tanks to 0°C. by means of a circulating glycol-water mixture chilled by Freon refrigeration (see p. 603). The compressor, brine chiller and pump are located in the doughmixer room. (See general plan, p.547). Nearby are the necessary controls with the exception of the reset button which is found in the blower room. The temperature of the circulating liquid is controlled by a thermostat which can be adjusted to give the proper temperature at the condensers. The temperature in the lines is read by inserting a thermometer in the wells located at various points in the system, while the temperature at the chiller is read on the Leeds and Northrup indicator in the doughmixer room. A Mercoid switch regulated by a thermostat in the cooling lines near the condensers (shown center right in photograph 5, p.580) controls a buzzer and gives warning should the refrigeration system fail and the temperature rise. The water to cool the compressor is filtered through two screens in parallel, which should be cleaned at regular intervals since failure of the water supply causes the compressor to overheat and shut off.

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

Usage Figures for Step 3

Tribnol (from Step 2)	ca. 27.5 lbs.	
$AlCl_3$ (charge for two columns)	68	
Chlorthane (theory from 51.6 lbs. 890A	53.1	
Chlorthane (actual	ca. 47 lbs.	ca. 99% pure
$AlCl_3$-AlF_3 Residue (Discharge from two columns)	ca. 50 lbs.	

Operational Procedure

The operation of the columns is quite flexible (see section below on "Variables and Variations"). The normal procedure described below is based on continuous operation using the Complex from five gallons of 890. In such a case one of the five-column set-ups is used with a full charge of 34 pounds of $AlCl_3$ in each column.

Normally the refrigeration system is left on, but if for some reason it is not, the pump and compressor should be turned on at least six hours before the start of a run.

The $AlCl_3$ is supported in the columns by glass wool held

on a tripod resting on the bottom flange. The $AlCl_3$ is charged through the hole in the top flange from the transfer cans provided for this purpose. The columns are tapped occasionally while loading to prevent formation of any air pockets.

About two hours before the start of a run, 8 lbs. steam pressure is admitted to all the jackets and thimbles and the vent line through the dry ice trap is opened into the hood. At this time the water should be turned on the dust traps, dry ice put in the dry ice trap, and the process line valves set to give the flow direction desired. We shall assume forward flow; i.e., 1-2-5 and 3-4-5. The temperatures of all the columns should be at least 100°C. before Tribnol is passed into the system.

When the columns are hot and the pressure in the manifold and kettle for Step 2 is equal to any back pressure built up in the columns on heating, the valves between the manifold and the column series are opened. At first the gas flow into the columns is held by means of needle valves at about 25 mm. on the "standard" flowmeter, provided, of course, the kettle will give that much flow. After 45 minutes, No. 1 condenser, by-passed at the end of the previous run, is cut into the system by the four-way valve. The above flow is maintained until condensate is seen in the sight glass under the Column 1 condenser. This usually takes about 15-30 minutes. Then the flow is raised gradually (20-30 min.) up to 70 mm. (0.8-0.9 lb. Tribnol per hr.). With the start of condensation the back pressures throughout the system will begin to drop. The pressure drop beyond the first column (i.e., 2 and 5) will decrease to nearly zero in about an hour. As soon as these pressures have dropped, the flow is raised to 140 mm. and kept there until the

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

PAGE 586eng-91

run is almost finished - 7-8 hours. At the same time the No. 2 condenser is cut in (Ref. 444).

During and before this period the course of the reaction in Column 1 is watched by following the "hot-spot" in the column. This is found by moving the thermocouple in the well in the column. When the hot-spot in the bottom of a column reaches 140-145°C., the by-pass around the steam trap on the lower jacket is opened, placing the lower half of the column on steam "blow". If the temperature falls below 130°C., 8 lbs. of steam is again admitted to the column jacket. This will probably happen as the hot-spot approaches the middle of the column.

About the time that the hot spot reaches the middle of the first column, the pressures in columns 2 and 5 will begin to rise and a fog may be seen in the sight glass of the first condenser. These are the first signs of a "break-through", i.e., incomplete conversion in column 1. Shortly thereafter condensate will be seen in the condenser of the second column. At this point the steam pressure in the lower jacket of Column 1 is raised to 60 lbs., the lower half of Column 2 is put on steam "blow", and condensation will continue in all condensers for a while but will gradually cease in Column.1. As soon as 40% of the condensation is seen dripping from the second condenser, the steam pressure in the lower half of Column 1 is raised to 80 lbs. and in the upper half to 60 lbs. During this period the hot spots in both columns are located and followed. The temperature of the first column is not important at this time unless it rises above 180°C., in which case the steam pressure should be reduced to prevent excessive sublimation of $AlCl_3$.

The observation of, say, 50% condensation from each column does not mean that 50% of the reaction is taking place in each column.

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

In fact when the condensation has completely stopped in the first column as much as 60% of the reaction may still be taking place in that column. This is due to the fact that the 40% of unconverted Tribnol carries the 60% which is converted as Chlorthane gas.

One hour after the steam pressure in the top of Column 1 is raised to 60 lbs., the pressure is raised to 80 lbs., unless there is already a good hot spot in the top in excess of 170°C. A hot spot should soon be found in the top half of this column, and occasionally a less intense one will also be found in the bottom half of the same column. The steam pressures should be regulated so that the hot spot in the top half of the column stays between 175-190°C. During this period condensation will begin again, or increase if it has never completely stopped, in the first condenser, at the same time gradually stopping in the second. After the hot spot fades and condensation stops again in the first condenser and begins again in the second, the series of columns should not be used for more than two hours at full flow. If the flow is dropping off due to the exhaustion of the charge in the kettle, as it will in a normal run, it is permissible to continue to use the series. But if the kettle reaction is not near completion (i.e., has not progressed so far that the temperature is rising in the pot), the series should be shut off until the purging of the system with air is started. (For the case where this happens in both column series, see below, section on "Variations", subsection 6, p. 593.)

When the reaction in the kettle is complete, air is passed through the kettle and into the columns at a rate of 20 mm. (See instructions for Step 2.) Before the air is turned on, however, the dry ice trap should be drained into the main storage tank and dry ice added

362

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

PAGE 588eng-91

if necessary. During the first part of this purging with air condensation will continue in the various condensers for half an hour or more. When it ceases in a condenser, the four-way valve at the top of the condenser is turned so that the condenser is by-passed, and the receiver below the condenser is then drained into the main storage tank while venting the main tank through the dry ice trap. The columns are left untouched during the blow through the kettle, and when that is stopped, they are cut off from the manifold. Then the column that is to be discharged (Column 1) is blown independently at the same rate for 2 hours or longer if necessary to make the total time of purging 7 hours. The steam on Column 1 is shut off after one hour of this blow.

When the air blow is finished, the dry ice trap is drained again and all the process line valves are shut. Before discharging the exhausted column the lines between the column and the trap are scraped out. Then the column is unloaded by removing the bottom flange and allowing the charge to drop out. It is usually necessary to pound the column and it may even be necessary to use a rod to loosen the charge if it is badly caked. The dust trap is only emptied every other time the column is discharged. A sample of the combined residues from column, lines and trap for each column is taken for analytical purposes after the residue has been weighed. New glass wool plugs are put in the column and trap, which should be closed up again as soon as possible.

As mentioned above, in a normal run two series of columns are used. In case the flow was 1-2-5 and 3-4-5, columns 1 and 3 will be exhausted at the end of the run. Columns 2 and 4 will be partially exhausted (10-20%) inasmuch as during the "break-through" some reaction was taking place in them. Columns 1 and 3 are discharged and reloaded

with fresh $AlCl_3$. Then during the next run, the flow will be 2-1-5 and 4-3-5. At the end of that run, columns 2 and 4 are discharged and reloaded. During the following run the flow will again be 1-2-5 and 3-4-5, etc.

Fresh water in the wash tower is charged every other run, the old water being saved until its analysis for 891 is checked.

In place of the usual chart showing the time requirements for Step 3, there is below a copy of a data sheet for a single run through one series. A log sheet for Step 2 is also included.

Variables and Variations

1. In normal operation with the equipment used above, an $AlCl_3$ column starts to "break through" when the charge has been only 40-45% reacted. However, for a considerable time after that the column will still convert a large percentage of the Tribnol passing through it. By using two columns in series it is possible to exhaust 80-85% of the $AlCl_3$ in the first column without danger of a "break through" (incomplete Tribnol conversion) in the second. Following such a procedure we normally start a run with the first column of the series partially exhausted and the second column fresh. The normal charge - 34 lbs. $AlCl_3$ - is such that in continuous operation using two two-column series with a common third, or safety column, the amount of Tribnol produced from 5 gals. of 890 is enough to complete the exhaustion of the first columns to the desired degree and leave the second columns in about the same condition as the first ones were originally.

2. The flow is kept low at the start of the reaction, to keep the back pressures from becoming too high, during which time

Table XII

Log Sheet for Typical Run - Step 3

RUN 80-39

COLUMNS Forward Flow

SERIES IV

CHARGE 3 - 4 34-3/16 lbs.

DISCHARGE 23-3/8 lbs. -

ANALYSIS: W=
Cl=

Date	Time	Flowmeter pressures mm.	#1	#2	#3	Column I (3) Bottom lbs.	Bottom Temp.	Top lbs.	Top Temp.	Column II (4) Bottom lbs.	Bottom Temp.	Top lbs.	Top Temp.	Remarks
2/14/46	1330	20				steam		5		5		5		Col. 4 by-passed
	1400	20												Through 3 and 4
	1500	20	6-1/8	5-1/4	2-1/2	9		10		7		8		
	1510	to 30												
	1525	to 48												Condensation in Col. 3.
	1600	to 96	4-1/8	2	1-1/8		138							" " " "
	1700	96	3	1-1/8	5/8		162							" " " "
	1800	103	3-3/8	1-3/8	3/4	blow	186							" " " " - sharp
														hot spot.
	1900	92	4-1/8	2-1/4	1-1/4		152							Condensation in Col. 3.
	1945	93	5-1/8	3	1-1/8	60				Blow				" " " 4.
	2000	96	5-1/2	3-1/4	1		144							10% condensation in Col. 4.
	2100	90	6-7/8	5-3/4	7/8	80		to 60	147					45% " " " "
	2200	91	9	6-3/4	1		160	to 80	162					85% " " " "
	2230	90					169		185					75% " " " 3.
	2300	62	6-1/4	3-5/8	3/4				189					55% " " " "
	2400	40	6-3/4	5	3/4				194					90% " " " 4.
	0100	20	4	3-1/2	3/4									100% " " " "
	0145	20												Air on kettle.
	0645	15												Fresh air on.
	0845													Air off.

(a) CCl_4 instead of Nujol was used in the flowmeter. A reading of 48 mm. equals a reading of 70 mm. on a standard Nujol flowmeter.

GOF 3692A PTD. IN U. S. A.

Table XIII

Log Sheet for Typical Run - Step 2
(Corresponds to Run of Table XII)

RUN 80-39

KETTLE #4

CHARGE 60.69 lbs.
DISCHARGE 28.94 lbs.
ANALYSIS
TRAP LIQUID 819 g.

		Kettle		Trap		
Date	Time	Temp.	Press.	Temp.	Variac	Remarks
2/14/46	1300				50	Start
	1500	184	7	229	"	
	1600	195	6-3/4	171	"	
	1700	198	6-3/4	185	"	
	1800	202	6-1/2	190	"	
	1900	202	6-1/4	192	"	
	2000	203	8	192	"	
	2100	206	10-1/2	183	"	
	2200	207	10	187	"	
	2300	228	7	206	"	Heat increased
	2400	303	6-3/4	248	"	
	0100	370	4-1/4	256	to 40	Air on
	0230	390		228	"	
	0330	400		214	"	
	0445	411		213	"	Heat off
	0645				"	Air off

Tribnol and Chlorthane displace the air, and to minimize the amount of products carried out as vapor with the air being displaced from the system.

3. At the start of the reaction the pressure ahead of the first column is quite high (5-7 lbs.), since there is gas flow throughout the system and the pressure here is the sum of the back pressures of all three columns. When condensation begins in the first condenser, the flow through the last two columns obviously is decreased and hence the pressure throughout the system decreases. When all the air has been purged from the first column, trap and condenser, and there is complete conversion in the first column, there is practically no flow through the last two columns and the pressures and pressure drops beyond the first condenser become nearly zero. When they begin to increase again, this is a sign of a "break through" in the first column - i.e., gas is again passing through into the following columns in the series.

4. The heating cycle for the columns is not necessarily rigid, but is based on the following considerations: While some reaction will occur at 75-80°C., a temperature of over 100°C. is needed to assure quantitative results at the start. Once the reaction is under way, the heat generated spontaneously raises the temperature of the lower part of the column. Hence it has been found that if this is allowed to become too high, the top half of the column will become caked and unreactive, presumably due to $AlCl_3$ subliming from the bottom portion. The temperature in the bottom half if therefore kept below 145° during the first part of the reaction. (See "Variables", 12, below and the log sheet of Table XII (p.590.)

One reason that a column "breaks through" when it is only partially exhausted is thought to be that the particles of $AlCl_3$ be-

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

PAGE 593eng-91

come coated with a layer of non-volatile AlF_3. Increasing the heat tends to break up these particles exposing the unused $AlCl_3$. When a column "breaks through", the bottom portion has been fairly well exhausted, and increased heating thus tends to increase its reactivity.

The final step in obtaining as complete reaction as possible is to heat the column above the active sublimation temperature of $AlCl_3$. This is not done until about 2 hours after the "break through", since heating the relatively fresh top half to the sublimation temperature results in a reaction so violent that there is danger of plugging the exit lines.

In the two hour "break through" period some of the $AlCl_3$ in the top half is reacted and therefore the reaction obtained upon raising the temperature is not so violent.

5. When the condensation stops for the second time in the first condenser, the first column is approaching the end of its usefulness and most of the conversion is accomplished thereafter in the second column. The two-hour time limit for full flow under these conditions is to prevent the possibility of the second column also "breaking through". If despite this precaution there is evidence that such a "break-through" is occurring, the series should be shut off as soon as possible.

6. In continuous operation it may be necessary to run on the second columns 4-5 hours to convert the Tribnol if there has been faulty operation in previous runs or the amount of Tribnol is excessively large (e.g. the "5 gal." batches of 890 received often weighed anywhere from 49 to 55 lbs.). In such a case the $AlCl_3$ in the second column is also well exhausted and therefore cannot be used in the next run. In this event the safest procedure is to discharge all the columns and recharge them with fresh $AlCl_3$. It should be remembered that each column

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

PAGE 594eng-91

to be dumped must always be blown with fresh air for two hours to recover the Chlorthane therein. If the $AlCl_3$ from the common third column is still free-flowing on discharge and if operation data for previous runs indicate that no break-through into this column has ever occurred, the residue may be recharged into one of the first columns.

7. The condensers are by-passed during the "blow", once condensation has stopped, since in continuous production it is necessary to purge completely only the first column and trap of each series. By leaving an atmosphere of Chlorthane in the condenser there is less air to be removed from the system at the beginning of the next run. This improves yields, since the air always carries out some Chlorthane. To carry out this idea it is also necessary to by-pass the condensers at the start of the run.

8. The condensers are cooled to only 0°C. to minimize the amount of Tribnol dissolved in the Chlorthane during a "break-through". While the vapor pressure of Chlorthane is rather high (ca. 450 mm.) at this temperature, a study of the back pressures has shown that very little Chlorthane passed on to the next column and that which went through the third column was caught in the dry ice trap. At this last point there should be no Tribnol present at any time. The small amount of material caught in the wash tower on the vent line testifies to the efficiency of this system.

9. If it is necessary to remove all the hold-up from the receivers, etc., the following procedure may be used. The normal procedure is followed up through the first part of the air blow. Then when during the blow the condensation stops, the receivers are drained as usual, but the condensers are not by-passed. Instead the cooling is turned off the

condensers and receivers and the blow continued for 4 hours after the receivers and condensers have warmed up above 12°C. (boiling point of Chlorthane). If necessary the blow may be cut off while they are warming up. The dry ice trap is then drained into the main storage tank and as much of the Chlorthane as possible blown from the storage tank to the distillation weigh tank. When this has been done, the dry ice is removed from the trap and the refrigeration cut off the storage tank. When these have warmed up, they are vented and then purged with air through a dry ice trap, or through the weigh tank and a dry ice trap.

10. The entire procedure outlined above has more or less assumed that everything runs well. It cannot be stressed too much, however, that such is not necessarily the case. Something out of the ordinary may happen in almost every run. If Step 3 is watched continually, though, and the unpredictables taken care of as they arise, no difficulty will be encountered. The three things to continually check are the flow rate, the pressures in the process line, and the temperatures in the reacting columns.

11. When two series of columns are used, the flow through each must be kept the same. Otherwise one series will "get ahead" (i.e., be more reacted) of the other, and the two columns of that series may both have to be discharged, which will lower the yield and lose time. The flow meters should therefore be kept clean and occasionally checked against each other to assure correct readings. In addition, since the pot pressure often varies 1-2 lbs. the flows should be continually checked to keep the desired flow. The flow rates should be carefully watched after the "break-through", since as the back pressure rises, the flow will decrease (it may even be necessary to raise the pot pressure by adjusting the automatic gas

controls to keep the flow up), and as the back pressure falls due to condensation returning to the first column, the flow will increase.

12. Most important of all in running the columns, one must keep an eye on the pressure gauges in the process lines. They give a good indication of what is happening inside the columns. As mentioned above (Variations 3), the pressures normally vary in a certain pattern during the run. This may be seen by noting the log sheet. At Time = 1500 the pressures were all rather high, but by Time = 1700, when most of the air was purged and there was good condensation, they had dropped considerably. They rose at the "break-through", dropped when condensation returned to Column 3, and rose again at the final "break-through". The values of these pressures are normal and any deviation from them must be looked into immediately.

The most common difficulty is with "plugs" which develop in the system. An increase in pressure not caused by an increased flow rate or a normal increase as mentioned above is a result of a plug. The first action taken is to locate the plug. If the pressure has risen in all five columns, the plug is either in Column 5, or the following lines, dry ice trap, or water trap. Such a plug is located by disconnecting the water trap, by-passing the dry ice trap, opening the line between the column and its trap and noticing which action lets out the pressure. Column 5 itself is plugged if all pressure remain high. If, however, the pressures on, say, columns 1 and 2 are high, but 3, 4 and 5 are normal, then the plug is somewhere in column 2, its trap and lines. If the pressure on just one of the first columns is high, that column, its trap or lines is plugged. Most frequently the "T", or line between a column and its trap, will be found plugged. This is easily remedied by shutting off the flow through that column, letting the pressure drop, and then opening the line and scraping out

the $AlCl_3$ which has sublimed up into it. Occasionally the plug is in the column itself. If this is the case nothing should be done if any sort of flow at all can be maintained in the column without exceeding 12 lbs. back pressure. If this cannot be done and the run is almost completed, the series of columns on this side should be shut off. Otherwise the column will have to be dumped and recharged.

Another common difficulty detected by the pressures is with "channels" in the column. The pressure differential through a column should be about 2 lbs., and if this drops to below a pound and there is flow through the column, a channel is developing. In this case the entrance and exit valves to the column should be shut off so that there is no gas passing through. The column should then be pounded up and down its length with a hammer. This procedure settles the $AlCl_3$ and fills the channels.

13. A glance at the log sheet above and the remarks on the temperature control of the $AlCl_3$ will show a slight discrepancy. Contrary to usual procedure the temperature in the lower half of Column 3 went up to 186°C.-far past 145°C. considered the safe limit for that stage of the run. Yet no difficulty was encountered. Steam pressure was shut off, and an attempt to cool the column with steam blow was made with no noticeable immediate effect. The line pressures were watched very closely, however, for signs of a plug which normally would have developed. There were no signs of a plug. If there had been, all steam to the column would have been shut off and the flow drastically reduced.

Whenever the reaction tends to get out of control, the procedure outlined below should be followed: (a) Reduce the steam pressure or put steam blow on the jacket surrounding the hot spot; or (b) completely shut off all steam on the column; or (c) reduce the flow.

GOF 3692A PTD. IN U. S. A.

Care should be taken, however, not to lose the hot spot, i.e., stop reaction completely. The steam pressure should be restored and flow raised before the "safe" temperature has been reached but after the column has definitely begun to cool, because experience has shown that otherwise the "hot spot will be lost" and never again regained.

Such a run-away hot spot is seldom encountered in the bottom half of the column, but is rather frequent in the top half when condensation returns to the first column after the break-through. The temperature should be kept below 190-200°C. On occasion the temperature has gone as high as 275°C. with no ill effects; on others a hot spot of 210°C. has caused the column to plug. In judging what action, and the urgency of such action, to take in case of a run-away hot spot, one should measure the width of the hot spot. For instance, the 186°C. spot mentioned in the data sheet was very sharp. That temperature was recorded at just one place and an inch to either side the temperature was 155°C. Such sharp hot spots represent but little danger if not allowed to spread. On the other hand, if they are 3-12 inches in width, the column will invariably plug.

Normally the hot spot will start at the bottom and creep up to the middle where it spreads and dies out. Then after the steam pressures have been raised, it reappears and travels up the top. Occasionally, however, the spot begins at the bottom and climbs almost to the top before the break-through and before the steam pressure is raised. In such cases condensation is rarely obtained again in the condenser of that column. Often if the column has behaved normally, but the steam pressures were not raised in time, condensation will never return to the first column or will return just as the run is finished.

GOF 3692A PTD. IN U. S. A.

14. In the winter the cooling water for the powder traps may be cold enough to condense Chlorthane. Evidence of such condensation is the lack of visible condensate in the sight glasses at a time when this should be seen and the abnormally low temperature of the bottom flange of the traps. This condition may be remedied by cooling the traps only intermittently when they become too warm.

GOF 3692A PTD. IN U. S. A.

Distillation

Distillation

Introduction

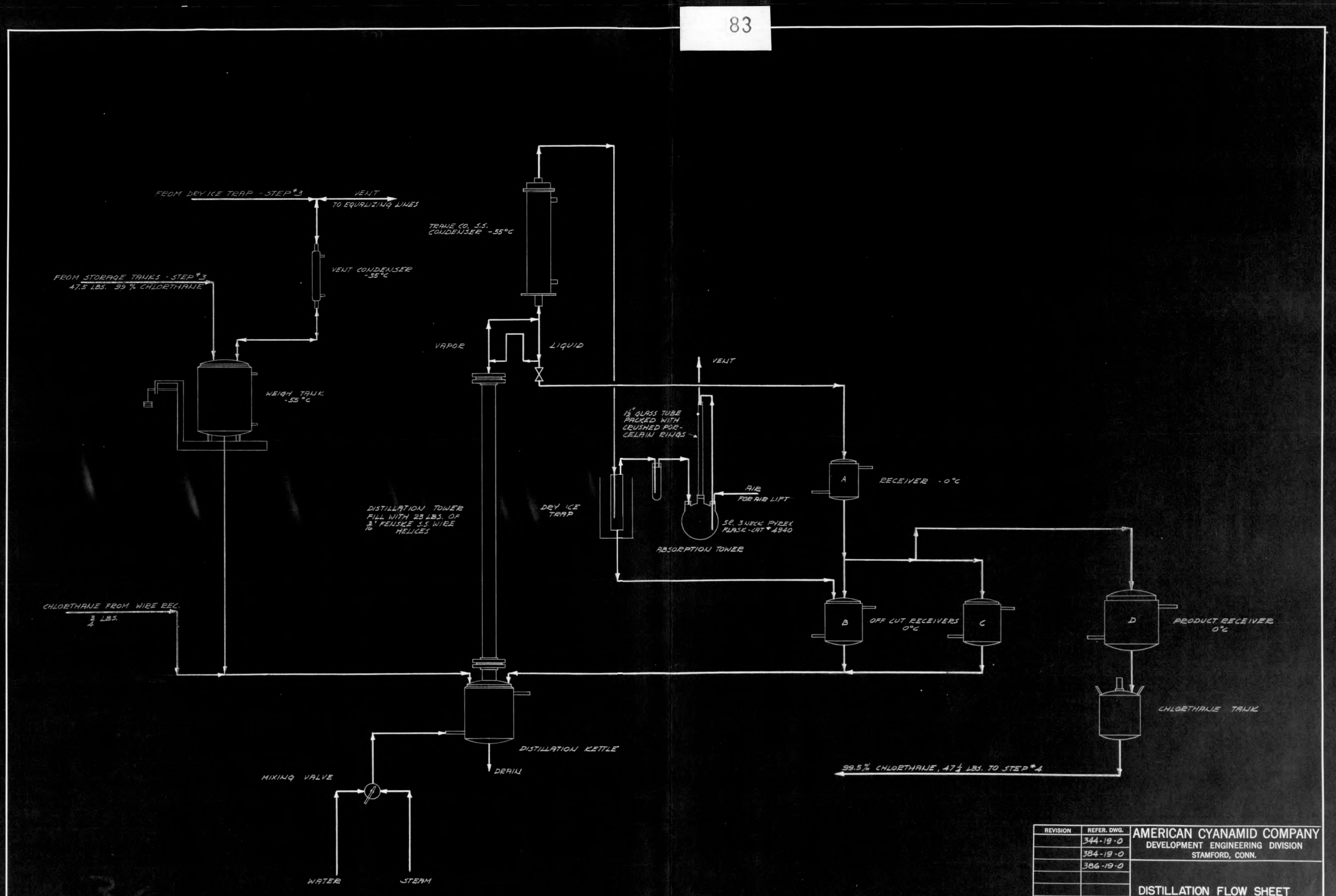
The Chlorthane blown from Step 3 to the distillation apparatus usually runs about 97.0 to 98.0% in purity. The impurities consist of ca. 1.0-1.5% low boiling liquids, 1.0-1.5% dissolved solids and a negligible amount of high boiling material. It is not easily determined what the contaminating compounds are by chemical analysis. The major part of the lower boiler material is dissolved Tribnol and silicon tetrafluoride with possibly some traces of other compounds, e.g. HF, HCl and other silicon compounds. The dissolved solids consist mainly of $AlCl_3$ and the oxide of 891 along with traces of other contaminating compounds like $FeCl_3$..

The dissolved solids are left behind in the still pot along with the high boiling residue, while the low boiling material is removed by fractionation. The purity can thus be raised to better than 99.5%. The silicon content of the distilled Chlorthane averages ca. 0.01 to 0.03%. The fluoride content is usually less than 0.1%.

Description of Distillation Equipment

The distillation set-up contains two separate units through which the Chlorthane is processed. The still is set up against the east wall of the center room of I. O. Building #2. (See Floor Plant, Dwg. 290-AA, p.545.) The various parts of the equipment, piping diagrams, flow sheet, etc. are shown on the following drawings.

82



REVISION	REFER. DWG.
	344-19-0
	384-19-0
	386-19-0

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

DISTILLATION FLOW SHEET

31-232-64

DESIGN: M.S. DRAWN: M.S.

SCALE: NONE

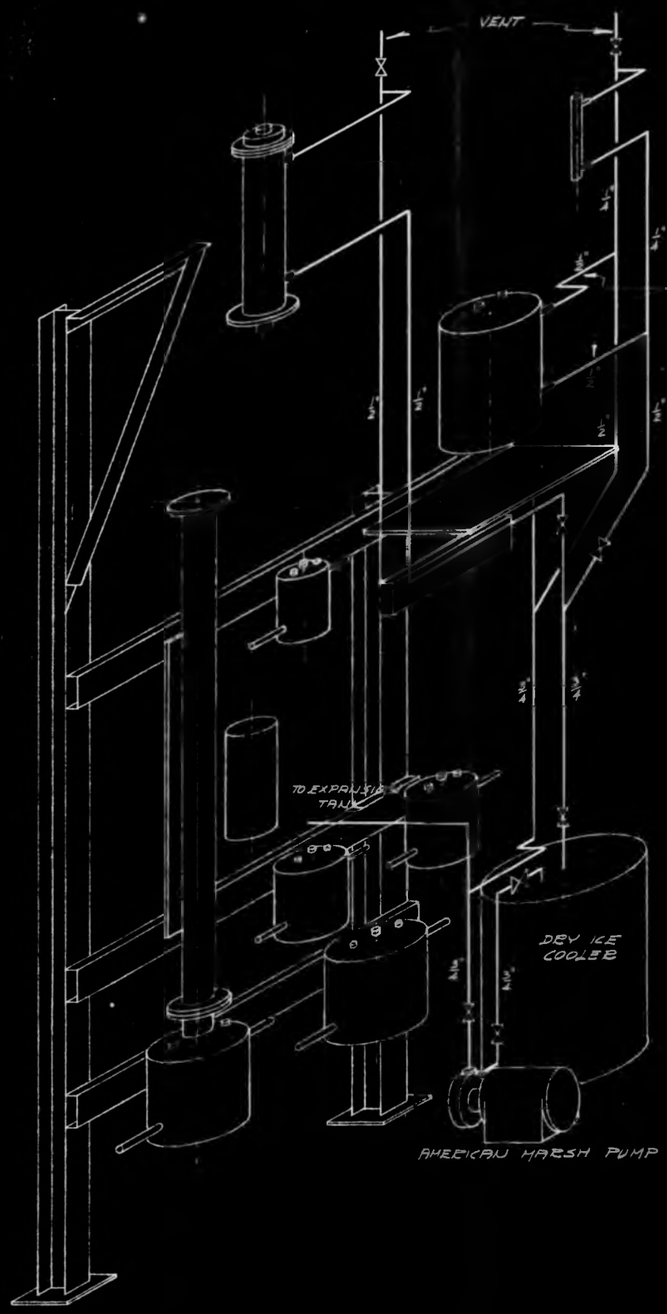
DATE: 6/24/46

DWG.	JOB	REV.
404	19	0

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

DECLASSIFIED



CIRCULATING FLUID TRICHLORO ETHYLENE (-55°C)

NOTES:
1. ALL PIPES & FITTINGS I.P.S. BLACK IRON
2. ALL VALVES BRONZE GATE
3. ALL PIPES LAGGED - 2" OF HAIRFELT

REVISION	REFER. DWG.
	108-9-0

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

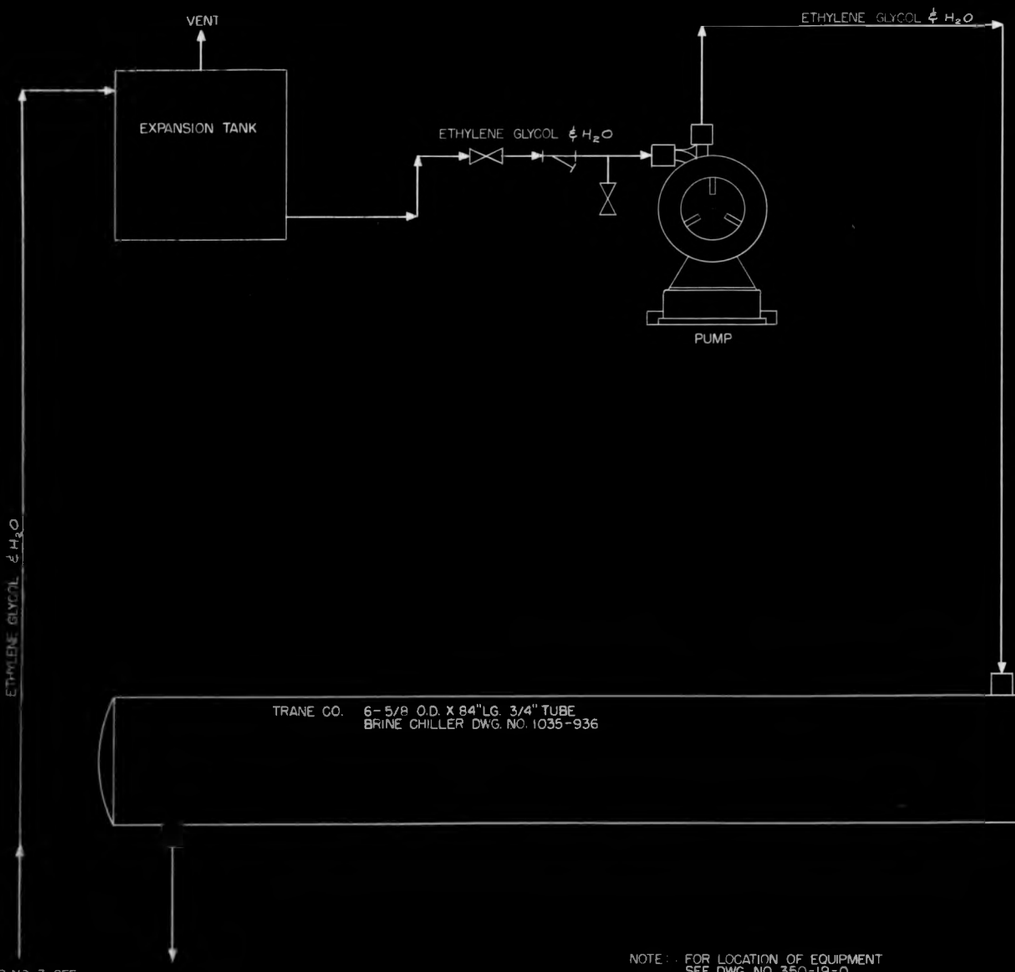
LOW TEMPERATURE COOLANT PIPING FOR DISTILLATION SYSTEM

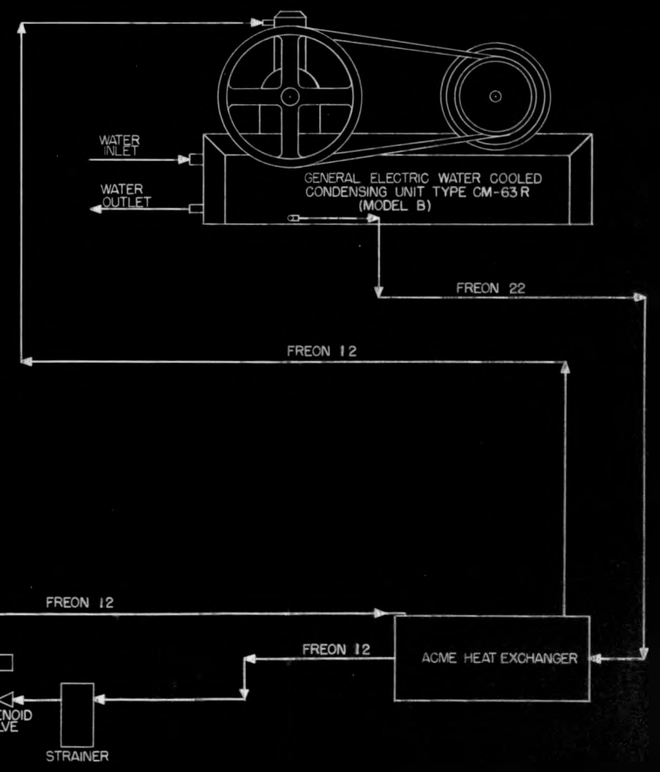
31-232-64
DESIGN: M.S.
DRAWN: M.S.
SCALE: NONE
DATE: 6/27/46
412 | 19

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

84





NOTE: FOR LOCATION OF EQUIPMENT SEE DWG. NO. 350-19-0

REVISION	REFER. DWG.
	350-19-0
	380-19-0
	401-19-0

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

HIGH TEMPERATURE REFRIGERATION SYSTEM FLOW SHEET

31-232-64

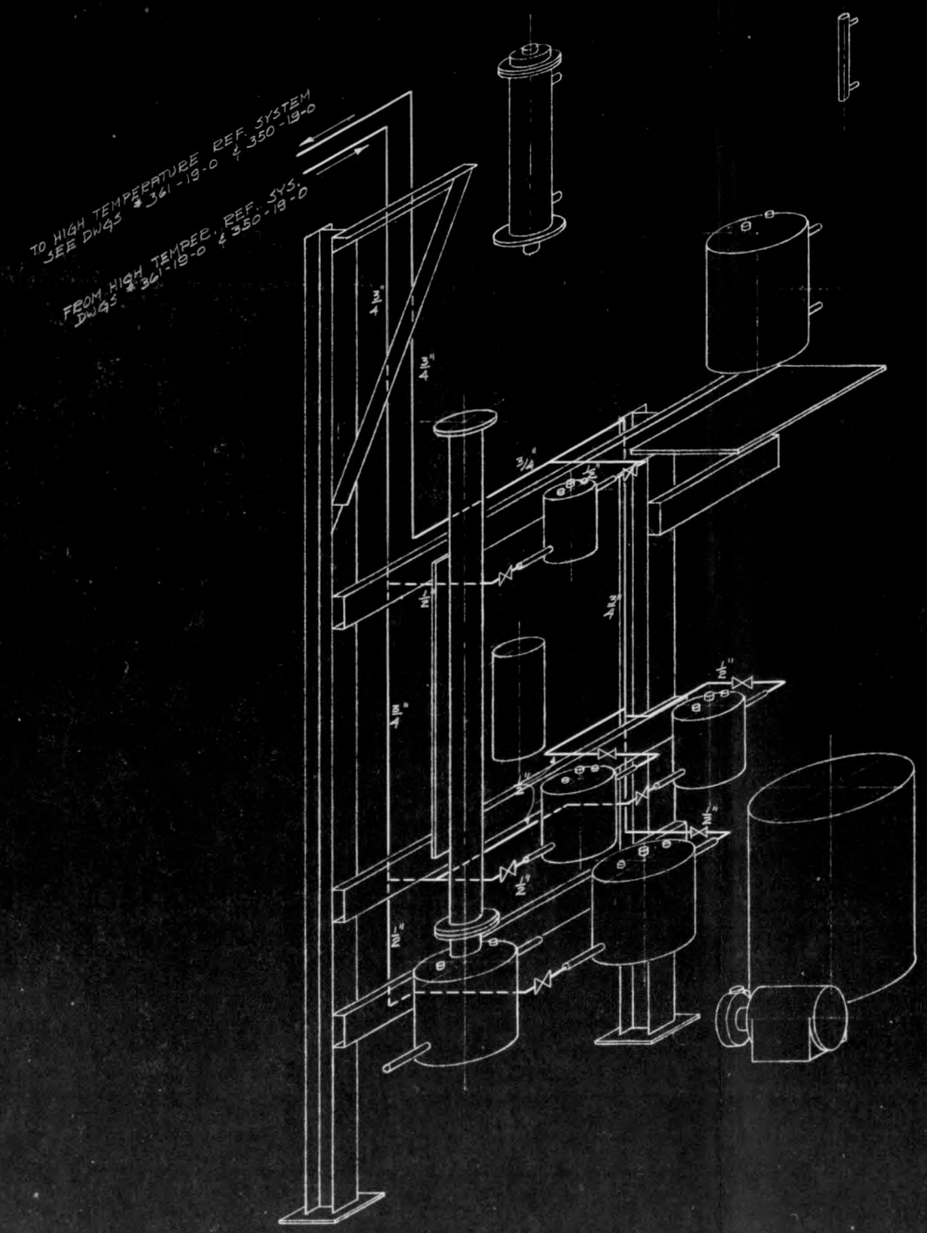
DESIGN: M.S. DRAWN: wel

SCALE: NONE

DATE: JUNE 12, 1946

DWG.	JOB	REV.
361	19	0

DECLASSIFIED



NOTES:
1. ALL PIPES & FITINGS I.P.S. BLACK IRON
2. ALL VALVES BRONZE GATE

REVISION	REFER. DWG.
	350-19-0
	361-19-0
	408-19-0
APPROVED	

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

HIGH TEMPERATURE COOLANT PIPING FOR DISTILLATION SYSTEM

31-232-64

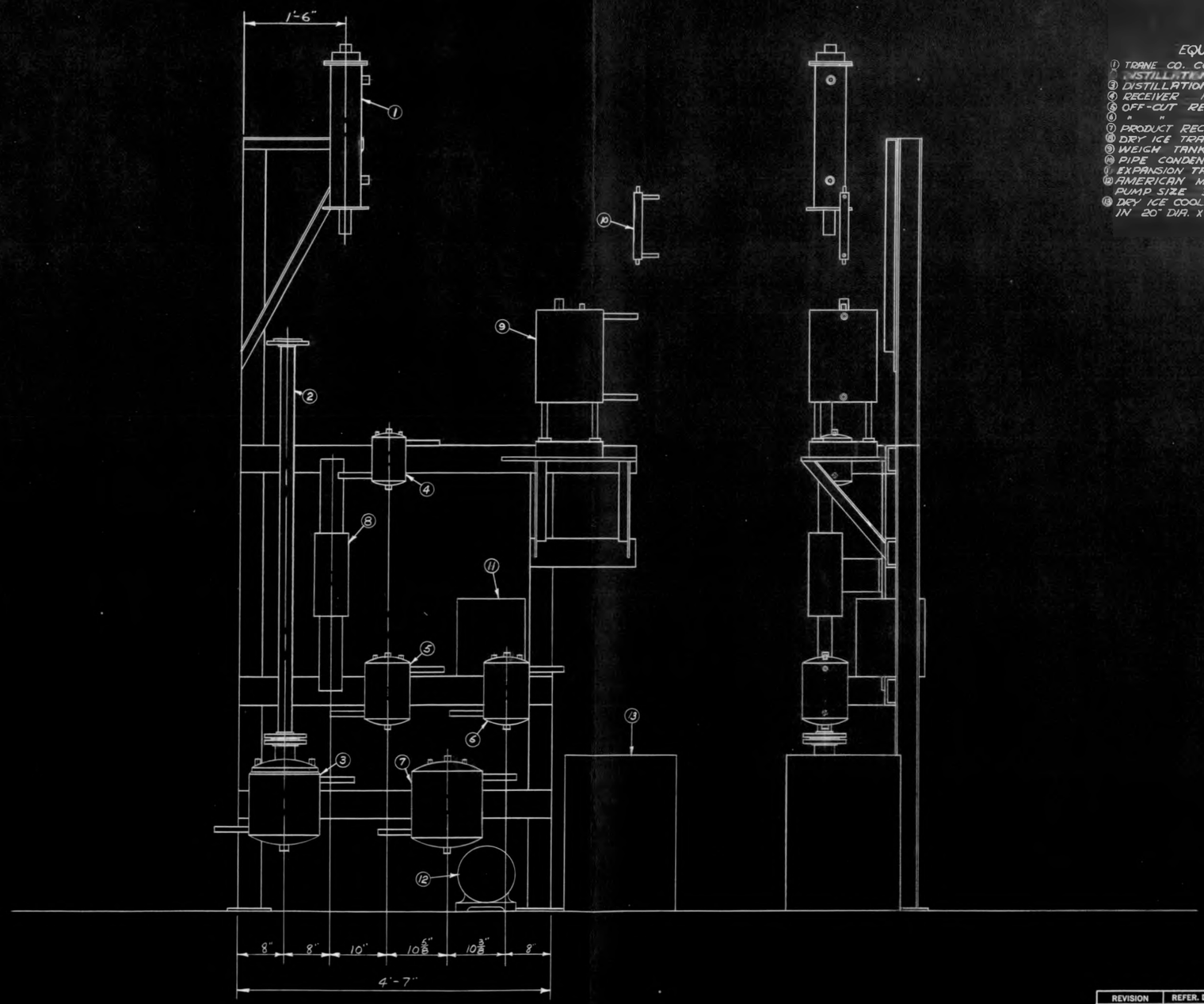
DESIGN: M.S.
DRAWN: M.S.
SCALE: NONE
DATE: 6/27/46

DWG.	JOB	REV.
401	19	0

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Problem No. 64.

87



EQUIPMENT LIST

①	TRANE CO. CONDENSER	DWG. #	1035/932
②	DISTILLATION TOWER	SEE DWG. #	410-19-0
③	DISTILLATION KETTLE	" "	#409-19-0
④	RECEIVER A	" "	#409-19-0
⑤	OFF-CUT RECEIVER B	" "	#409-19-0
⑥	" " " C	" "	#409-19-0
⑦	PRODUCT RECEIVER D	" "	#409-19-0
⑧	DRY ICE TRAP	" "	#410-19-0
⑨	WEIGH TANK	" "	#410-19-0
⑩	PIPE CONDENSER	" "	#410-19-0

⑪ EXPANSION TANK 5 GAL. CAPACITY

⑫ AMERICAN MARSH PUMP CO. TYPE V TURBINE PUMP SIZE 31A50 DWG. #W9309

⑬ DRY ICE COOLER - 10 COILS OF 3/4" PIPE 18" DIA. IN 20" DIA. X 28" DRUM

REVISION	REFER. DWG.
	407-19-0
	409-19-0
	410-19-0

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

DISTILLATION SYSTEM LAYOUT

31-232-64

DESIGN: M.S. DRAWN: wel

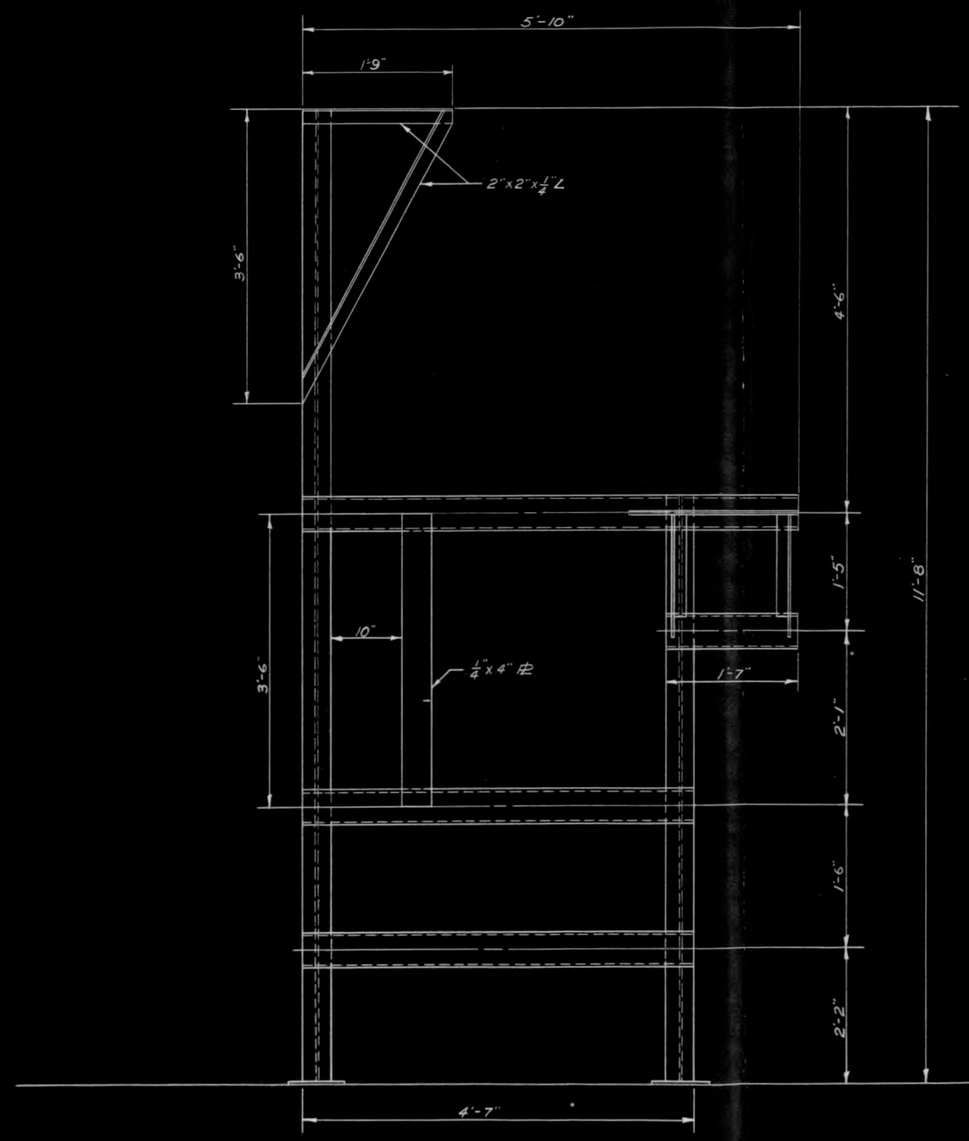
SCALE: 1" = 1 FT. DWG. # 408 19

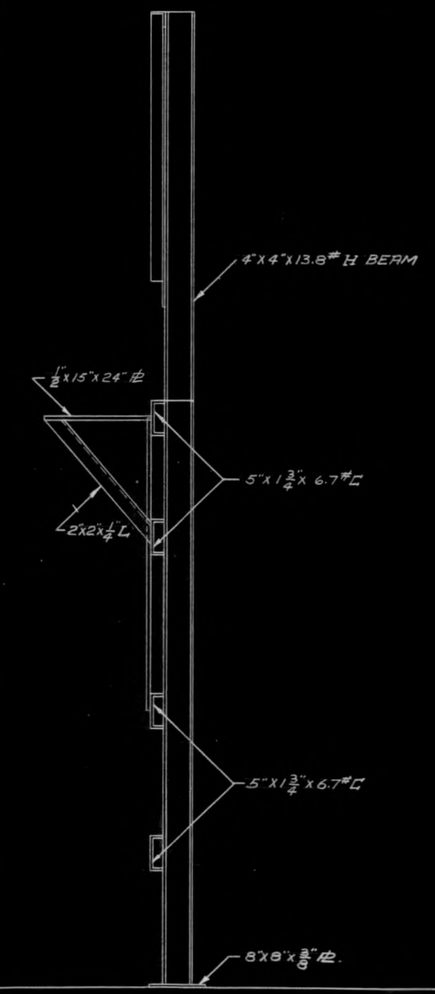
DATE: 6/24/46

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 232.
Program No. 64.

87





REVISION	REFER. DWG.
	408-19-0
APPROVED	

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

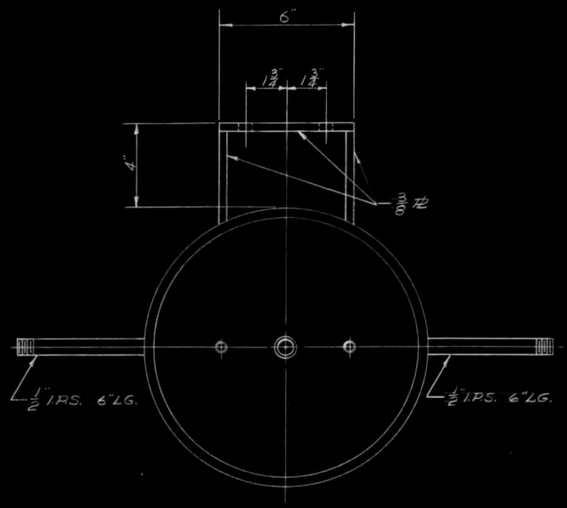
FRAME FOR
DISTILLATION SYSTEM

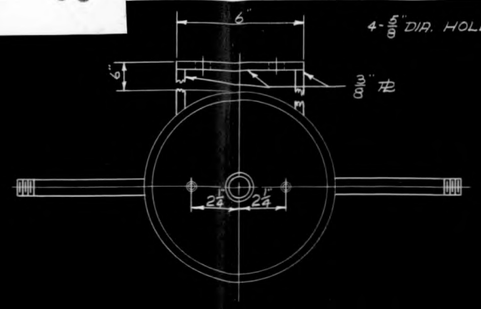
31-232-64

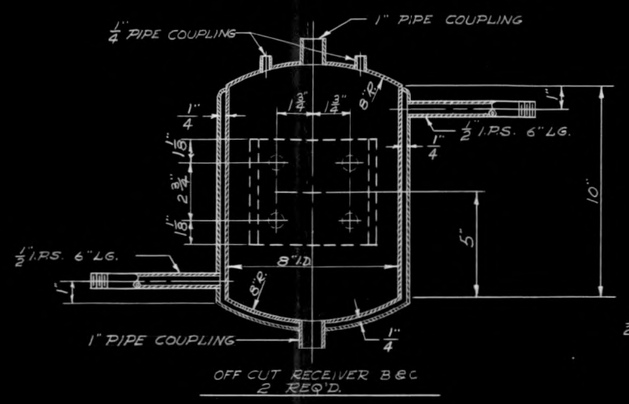
DESIGN: M.S.	DRAWN: wel
SCALE: 1" = 1 FT.	DWG. 407 / JOB 19 / REV. O
DATE: 6/24/46	

30

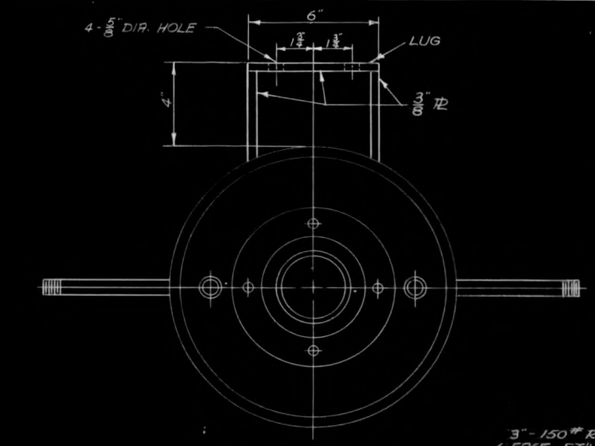
DECLASSIFIED

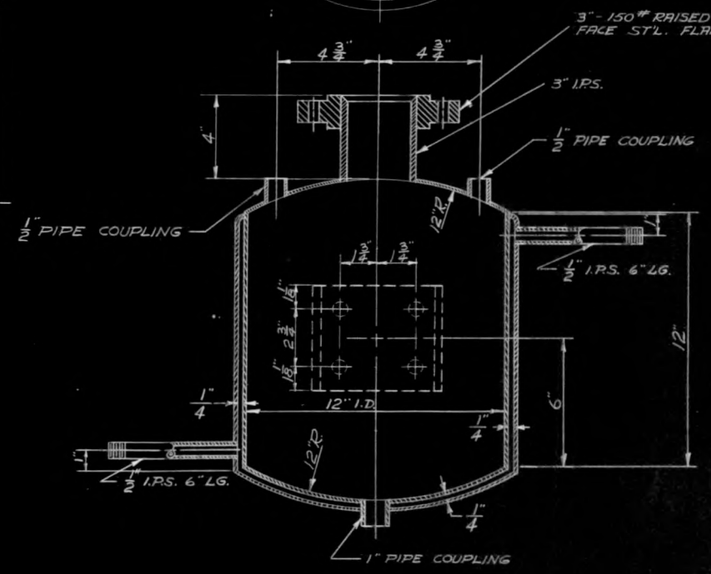




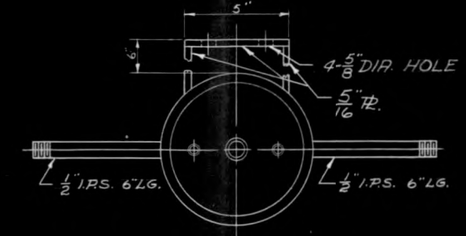


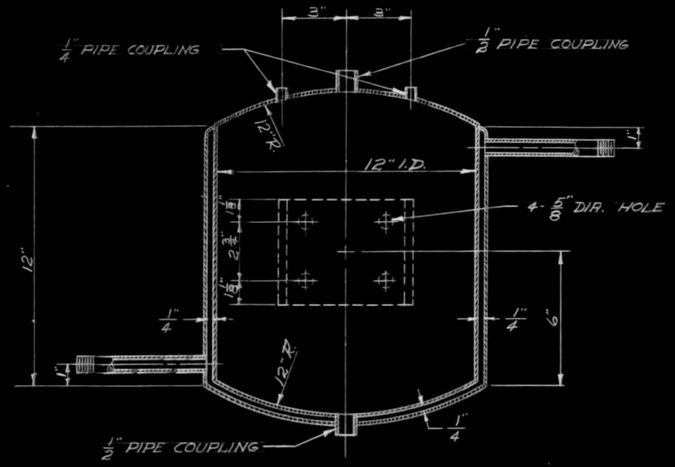
OFF CUT RECEIVER B&C.
2 REQ'D.



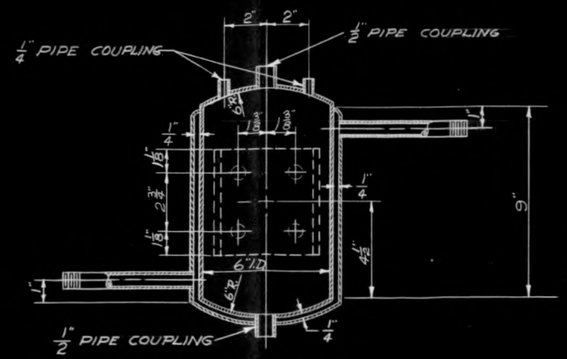


DISTILLATION KETTLE
TANK & JACKET TO BE MADE OF #10 GA. BLK. IRON
1 REQ'D.





PRODUCT RECEIVER D
1 REQ'D.



RECEIVER A
1 REQ'D.

NOTE: RECEIVERS A, B, C & D TO BE MADE OF #10 GA. 18:8 S.S.
JACKETS - #10 GA. BLK. IRON
COUPLINGS - STAINLESS ST'L.

REVISION	REFER. DWG.
	408-19-0

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

AUXILIARY EQUIPMENT
FOR DISTILLATION SYSTEM
SHEET NO. 1

31-232-64

DESIGN: M.S. DRAWN: wel
SCALE: 3"=1FT.
DATE: 3/26/[illegible]

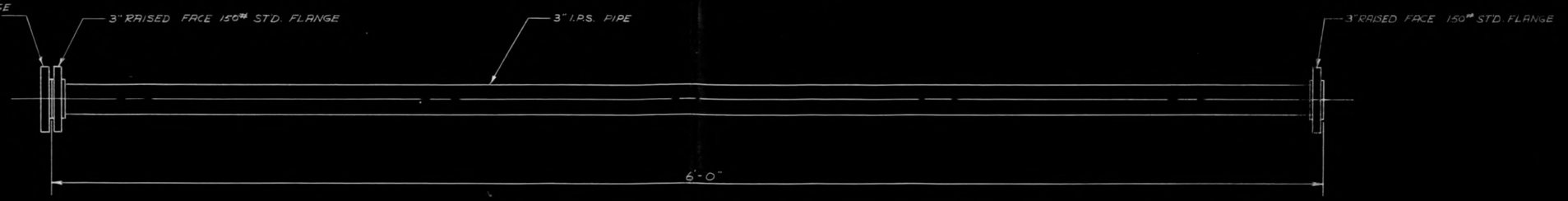
DWG.	JOB	REV.
409	19	○

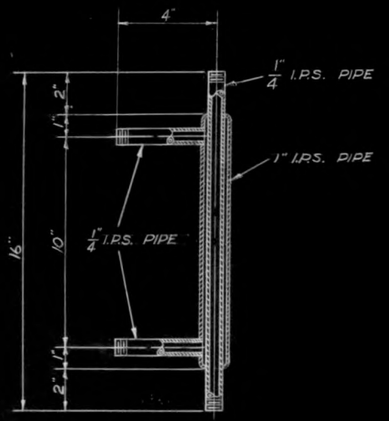
AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 238.
Problem No. 64.

89

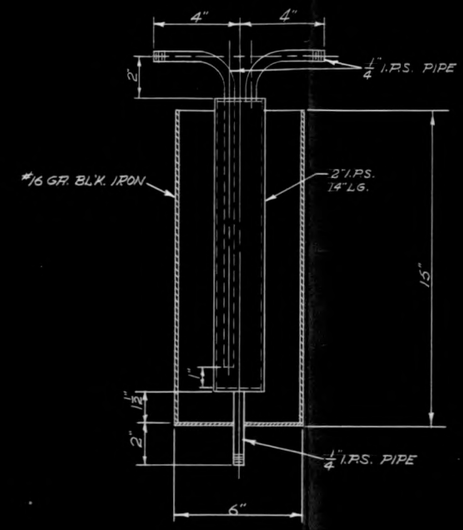
DECLASSIFIED



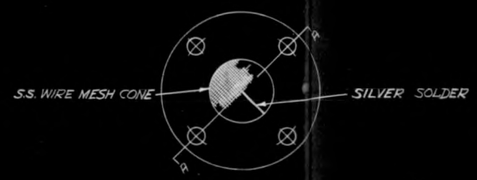


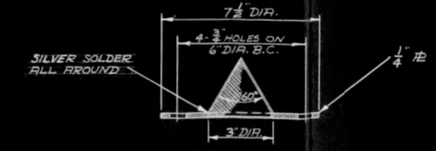
CONDENSER
MAT. BL'K. IRON - 1 REQ.
SCALE 3"=1 FT.

DISTILLATION TOWER
MAT. 18:8 S.S. - 1 REQ'D.
SCALE - 1 1/2" = 1 FT.



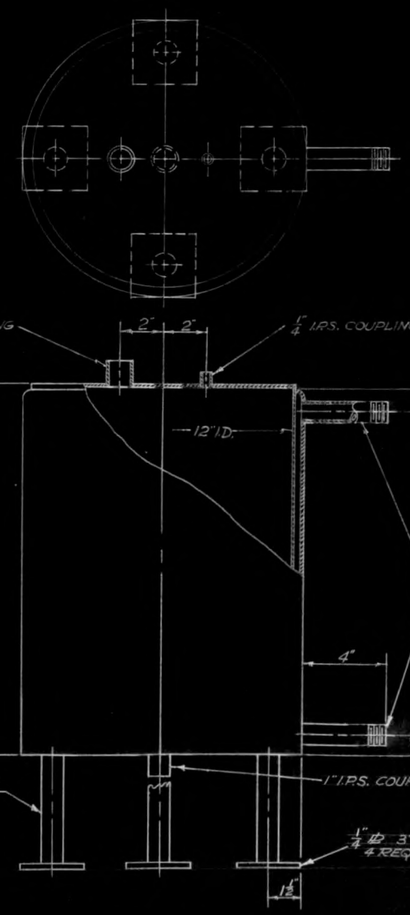
DRY ICE TRAP
MAT. 18:8 S.S. - 1 REQ'D.
SCALE 3"=1 FT.





SECTION A-A

PACKING SUPPORT
MAT. 18:8 S.S. - 1 REQ.
SCALE - 3"=1 FT.



WEIGH TANK
MAT. BL'K. IRON - 1 REQ.
SCALE 3"=1 FT.

3250

REVISION	REFER. DWG.
	408-19-0
APPROVED	

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

AUXILIARY EQUIPMENT FOR DISTILLATION SYSTEM SHEET NO. 2

31-232-64

DESIGN: M.S. DRAWN: wel

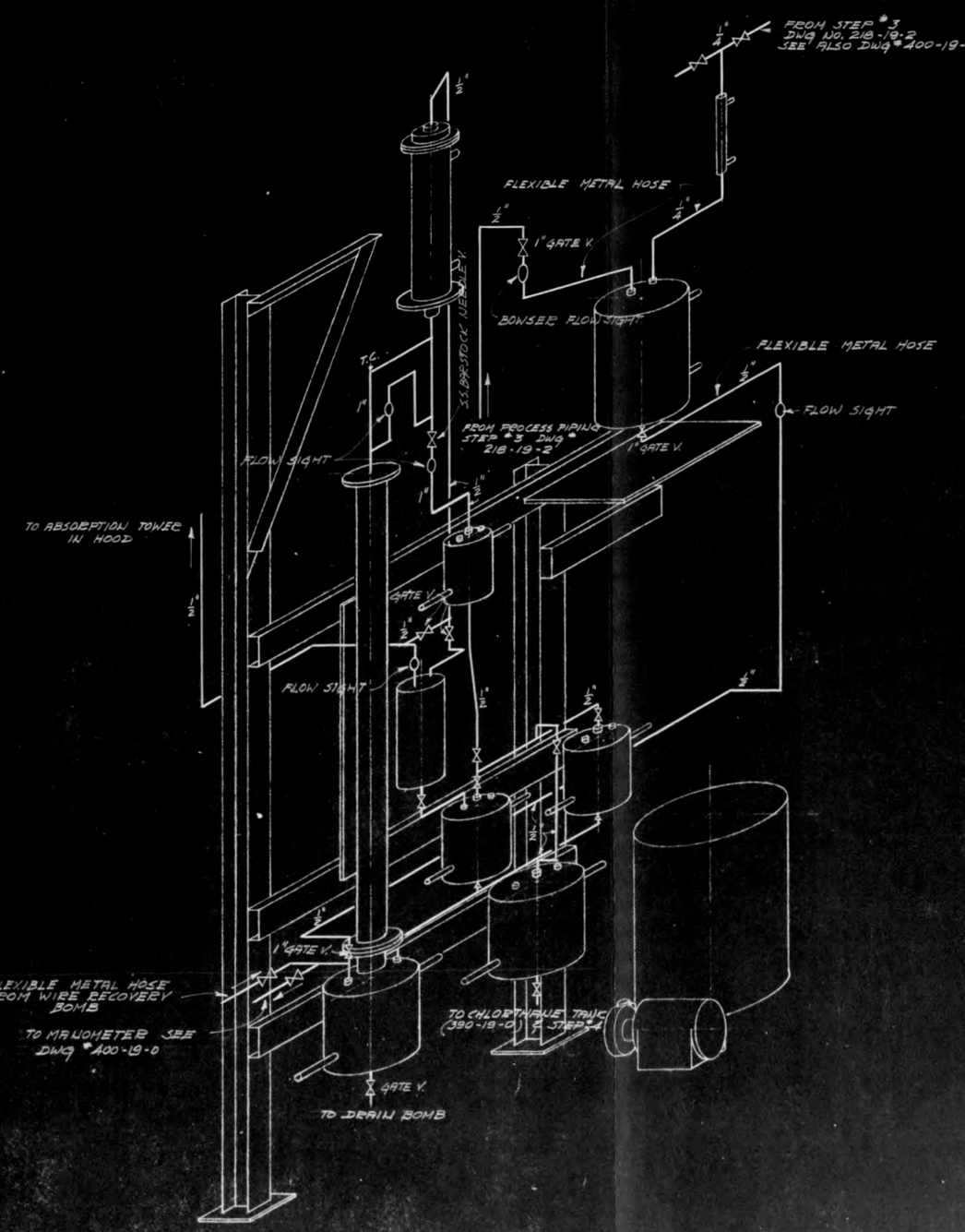
SCALE: AS SHOWN

DATE: 6/27/46

DWG.	JOB	REV.
410	19	0

DECLASSIFIED

DECLASSIFIED



NOTES:

ALL TANKS EQUIPPED WITH LIQUID LEVEL GAUGES

ALL PIPES AND FITTINGS I.P.S. STAINLESS STEEL

ALL VALVES BROWNE GLOBE NEEDLE EXCEPT WHERE NOTED

REVISION	REFER. DWG.
	218-19-2
	400-19-0
	404-19-0
	408-19-0

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

PROCESS PIPING FOR DISTILLATION SYSTEM

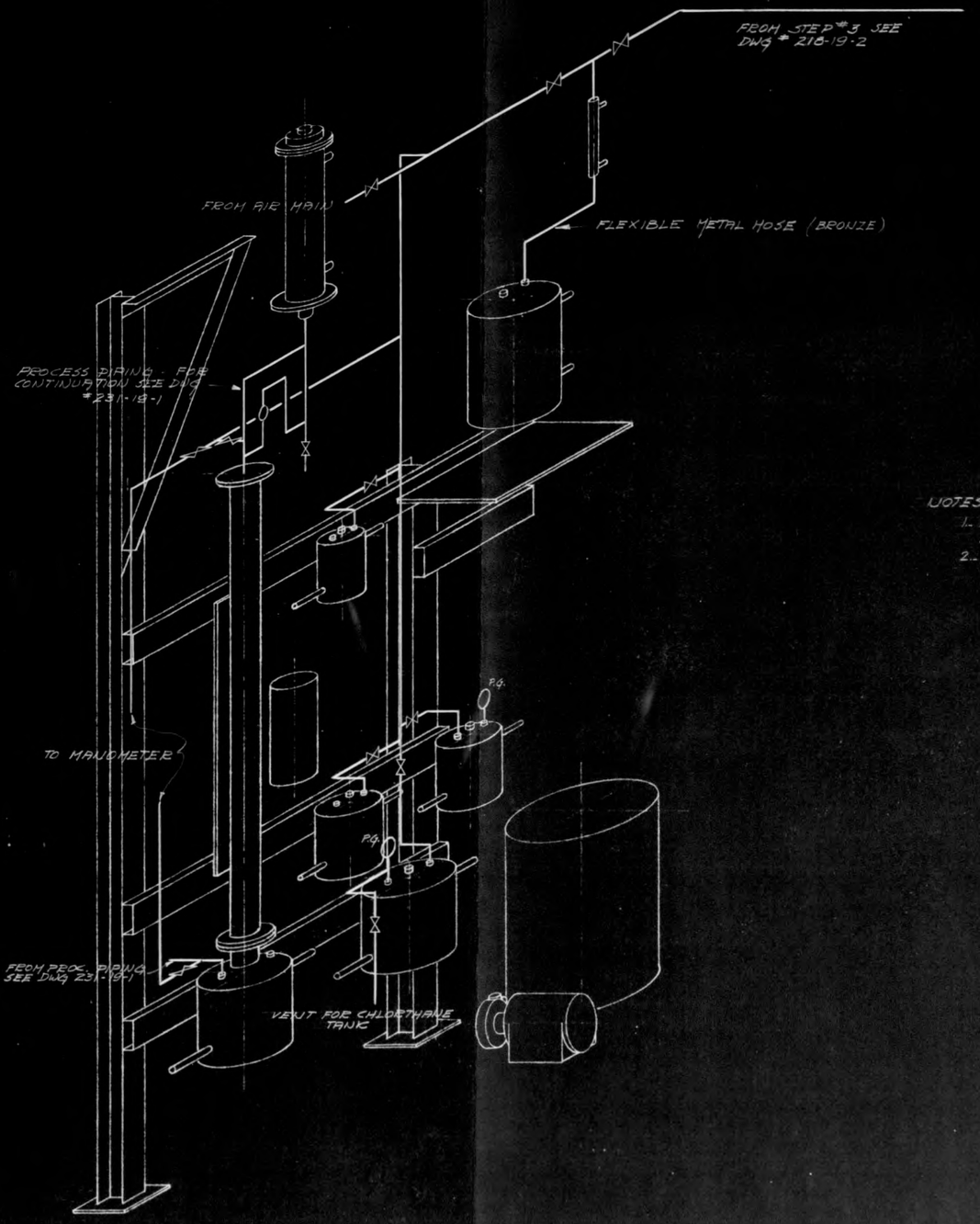
31-232-64

DESIGN: M.S.	DRAWN: M.S.		
SCALE: NONE	DWG.	JOB	REV.
DATE: 6/26/46	231	19	1

AMERICAN CYANAMID COMPANY
Stamford Laboratories

609 eng 91

Investigation No. 232.
Problem No. 64.



NOTES:
1. ALL PIPES & FITTINGS ¼" I.P.S. BLK IRON
2. ALL VALVES ¼" S.S. BARSTOCK NEEDLE VALVES

REVISION	REFER. DWG.
	231-19-1
	218-19-2
	404-19-0
	408-19-0

APPROVED

AMERICAN CYANAMID COMPANY
DEVELOPMENT ENGINEERING DIVISION
STAMFORD, CONN.

EQUALIZER PIPING FOR DISTILLATION SYSTEM

31-232-64

DESIGN: M.S. DRAWN: M.S.
SCALE: NONE
DATE: 6/27/46

DWG.	JOB	REV.
400	19	0

AMERICAN CYANAMID COMPANY
Stamford Laboratories

Investigation No. 252.
Problem No. 64.

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

The Chlorthane is first blown over by air pressure from one of the storage tanks of Step 3 into the weigh tank where it can be weighed to the nearest ounce. It is then allowed to drain into the still pot, where it is fractionated to get rid of the 1.0% or more of low boiling material, the residue, and high boiler material.

The weigh tank consists of a 4-5 gallon, jacketed, black iron tank on a small Fairbanks Scale. Connections to the weigh tank are of flexible copper tubing. The jacket is cooled by trichlorethylene circulated from the same dry ice cooler that is used to cool the distillation column condenser.

The Chlorthane is drained from the weigh tank through a flow sight glass to observe the rate of draining.

The distillation apparatus itself consists of a black iron still pot of five gallons capacity with a steam jacket, a 3" diameter stainless steel column of 6' length which is filled with 3/16 " diam. stainless steel Fenske helices, a stainless steel condenser and reflux splitter, and four jacketed receivers for the various fractions. The condenser head is kept at ca. -55°C. by trichlorethylene circulating through a dry ice cooler. The reflux splitter is controlled manually through visible observation of the reflux and distillate streams through two flow-sight glasses.

The rate at which Chlorthane can be distilled is determined by the reflux ratio. When using a reflux ratio of 10:1 to 20:1 in the separation of the first cut, a distillate rate of 10 lbs./hr. can be obtained. A lower reflux ratio of 3:1 or 5:1 is usually used in the takeoff of the main cut. A distillate rate of 20-30 lbs./hr. is easily obtainable with the lower ratios.

Fenske states that the height equivalent to one theoretical

plate may be about equal to the column diameter when operating at atmospheric pressure. If this holds for Chlorthane during separation of its impurities, the number of plates would be 24. There is probably efficient separation of low boilers in the column. In order to remove close-boiling high boilers it would be necessary to discard more off-cuts, which was not done. It is believed the salts and very high boilers were removed effectively. This phase of purification might be improved upon, but results in subsequent steps do not indicate the need for this.

Operational Procedure

The first step in getting the still into operating condition is to check the circulation of the glycol-water system through the jackets of the four distillate receiver tanks by nearly closing one of the jacket valves on each tank and listening to the resulting hissing if the circulation is good. The temperature of this system, as measured on the main outlet from the tanks by means of a thermocouple, should be less than 0°C. if the system is working correctly. Ordinarily, the glycol-water system needs no attention other than cleaning the water filter on the refrigerating machine once weekly.

The dry ice-trichlorethylene refrigerating system is started next by turning on the pump and letting all the air in the system work out through the surge tank or through the air vent valves above the condenser outlet and the weigh tank outlet.

If the weigh tank is to be used first (as it would be ordinarily), all of the circulation is forced into the weigh tank jacket by use of the proper valves. Dry ice is added slowly to the coil cooler in order not to boil out any of the trichlorethylene in the cooler. A vent to the nearby hood takes care of the CO_2 gas. The dry ice can be dropped into the cooler in rather big chunks of 10 lbs.

QOF 3692A PTD. IN U. S. A.

or more. This will give a temperature of ca. -55°C. After the boiling in the coil cooler has subsided to a large extent, more dry ice is added until two-thirds full.

It usually takes one-half hour for the weigh tank to become thoroughly chilled. The temperature of the outlet from the weigh tank is measured by a thermocouple. After the temperature has become constant, the weigh tank is weighed. This weight should not change even by one ounce over a period of 15 minutes. The final weight is entered on a prepared data sheet.

While the weigh tank is being cooled, other matters can be given attention. All of the valves leading from the weigh tank should be closed including the valve on the blow line, the air vent valve, the drain valve, and the Step 3 vent valve. The latter valve may be one of several possible ones but it is best to use the valve actually leading into the dry ice trap at Step 3 (of either set).

The Chlorthane is blown over from one of the storage tanks at Step 3 by means of dry air. (Consultation with the operator of Step 3 is wise at the time.) All exits of the storage tank are closed and 16 lbs. of air pressure put into the tank. The drain valve at the storage tank is opened and then the blow line valve above the flow sight glass at the weigh tank is opened. The Chlorthane will not come over immediately, since it has to cool the blow line pipe, but eventually it will. After it stops, the blow line valve is closed and the vent valve at Step 3 is carefully vented to relieve the air pressure in the weigh tank. Much use can be made of the pressure gauge on the weigh tank. Usually the pressure will decrease somewhat without venting through condensation of some gas.

GOF 3692A PTD. IN U. S. A.

AMERICAN CYANAMID COMPANY
STAMFORD LABORATORIES

INVESTIGATION NO. R. U. 232.
PROBLEM NO. 64.

PAGE 614eng-91

By repeatedly putting 16 lbs. pressure on the storage tank and repeatedly blowing and venting, all of the Chlorthane can be blown over. No more than 50 lbs. of Chlorthane should be put into weigh tank at any time. After the first venting it is not necessary to vent much after the second or third blow, since most of the air in the weigh tank is flushed out with the first venting. A rapid loss of pressure in the storage tank and a rapid build-up of pressure in the weigh tank is a certain indication that there is no more liquid in the storage tank. The weigh tank weight is then read and entered on a distillation data sheet along with the batch number.

The next step is getting the still itself into operation in order to receive the volatiles from the flash pot. The trichlorethylene system is cut off from the weigh tank and the circulation forced through the condenser of the still. This is done carefully to avoid boil-over of the dry ice cooler fluid. The distillate takeoff valve should be closed and the main valve for all the vent lines leading from the receiver tanks to the still head should be only partially open. The vent line from the condenser to the absorption tower in the hood should be open.

The dry ice trap in the vent line from the top of the condenser should be filled with dry ice carefully and the valves set so that the flow of gas is through it, with the bottom valve shut.

The Chlorthane may then be drained to the still pot by opening the drain valve and vent line to the still head. This must be done carefully with constant observation of the still manometer to prevent excessive pressure and blow-out of the manometer.

GOF 3692A PTD. IN U. S. A.

After all of the Chlorthane has been drained from the weigh tank, the drain valve is closed. It is at this point that any previous off cuts in tanks B and C can be drained into the still pot if the liquid level gauge indicates that there is space for it. A good reflux is started in the still by turning on the steam and water mixer so that the hot water is about 25-30°C.

At the same time the dry ice is removed from the coil tank so that the circulating trichloroethylene will warm the still head condenser. This warm-up is continued until the trichloroethylene is at about -10°C. During the warm-up the dissolved gases and the low boilers are volatilized and pass out through the vent at the top of the still, through the dry ice trap, and thence to the absorption tower in the hood. The dry ice trap catches most of the Chlorthane that comes over and may fill up, as indicated by the appearance of liquid in the sight glass above it. If this happens before the temperature has reached -10°C., the trap must be drained and the warm-up continued.

When the temperature reaches -10°C. dry ice is added to the coil tank and the trap is drained to receiver B. The heat to the still is increased and the fore-cut takeoff started as soon as a good reflux is established. A reflux ratio of 10-1 to 20-1 should be used. The fore-cut takeoff into A tank is continued until the four junction thermocouple at the still head shows 11.2°C. This usually requires that 8-10 lbs. of Chlorthane be collected. The forecut is drained to B or C tanks and the valves to them closed. The main cut is taken with a reflux of 3-1 to 5-1 until there is only about 1/2" of liquid left in the still or until the still head temperature rises above 12.3°C. The still is then shut down.

In shutting down, the inlet and equalizing lines to the product tank D must be closed as must the valves to the manometers. Then the product take-off valve and other valves leading to tanks A and to B or C should be opened and left open so that any Chlorthane left in the system may work over to the refrigerated tanks and condense. The vent valve in the hood must be closed also. A drain bomb, like the storage bomb shown on Drawing No. 403-19-0, p.732, fitted with a union and elbow, is laid on its side on the floor under the still pot and connected to the 1" connection on the bottom. The 1/4" pipe is connected to the still by means of the flexible metal hose used for charging Chlorthane from wire recovery, etc. With all valves then opened the remaining Chlorthane and solids run down into the drain bomb. After a few minutes the valves may be shut and the bomb removed and weighed. While this bomb is draining the cooling system may be shut down.

Mention was made of adding Chlorthane through the flexible metal hose to the still. When contaminated Chlorthane from Step 4 is brought in for redistillation, the bomb holding it is connected to the still pot by the flexible metal hose and the bomb is put in a hot water bath to drive out the crude Chlorthane. The same procedure is followed with crude Chlorthane from wire recovery and with the Chlorthane from the still drain bomb. In the latter case the solid residue builds up in the drain bomb and when about 10 lbs. has accumulated it is washed out with steam and hot water. The bomb is dried carefully before reuse.

The absorption tower connected to the still head vent consists of a three-neck flask with a packed tower connected through one of the necks. An air lift takes the water out of the flask and

pumps it to the top of the tower. This water is changed whenever it becomes too viscous to pump or too saturated to absorb any more Chlorthane. The solution is very corrosive and will cause bad burns as it contains fluoride ion.

The Product Chlorthane is collected in D tank. When the Chlorthane is needed in Step 4 one of the bombs shown in Dwg. 390-19-0 is connected to the bottom of D tank by means of the union provided. An equalizing connection, shown in Dwg. No. 400-19-0, p.610 is also connected to the bomb. The bomb is cooled with a little crushed dry ice piled around it and all four valves are opened. A calibration curve of the level of Chlorthane in D tank vs. weight enables the correct weight, 40 lbs., of Chlorthane to be drained into the bomb. After the required weight of Chlorthane has been drained, all the valves are shut except the liquid line valve on the bomb. Then the line between the two liquid valves is heated with a burner in order to drive out any liquid Chlorthane. After the line and union are hot the valve is shut, and the union may be opened without loss of material. The bomb is then weighed and the exact weight recorded.

The by-products of the distillation are the solid residue in the drain bomb and the absorption wash water, both relatively rich in 891A. The wash water may be evaporated under a water-jet induced vacuum in a Corning Distilling Apparatus #3460. This yields crystals, "Oxide", containing approximately 10% 891A when dried. By using vacuum distillation and a water jet pump the fume disposal problem is eliminated. When the drain bomb is washed out the water can be filtered and the filtrate evaporated as above. Both filter cake and filtrate crystals contain around 10% 891A. The "Oxide" can be used

in the process in either of two ways. It may be made into "Salt" by a process similar to that used for recovered 890A (see section of this report on 890A Recovery) or it may be added directly with the "Salt" to the "Salt Recovery", in which case more acid is required. For a more complete discussion of this, see Ref. 507, 508.