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MU-1780 (Rev. 3/78)

(15)

E. I. DU PONT DE NEMOURS & COMPANY
Pigments Department

SERIAL NO.: KN-69-12
COPY No.: 15

KN-69-12

NEWPORT PLANT
PIGMENT COLORS RESEARCH REPORT

SUBJECT: CONTINUOUS GMC SYNTHESIS

PERIOD COVERED: OCTOBER, 1968 - SEPTEMBER, 1969

SERIAL NO.: KN-69-12

DATE: 9/11/69

KN-69-12

COPY NO. 15

1. Numerical File - 223.4
2. Research Office File, Newark - 223.4
3. Newark Library File - 223.4
4. M. Hunt/E. Gonick - Wilmington
5. W. S. Struve - Newark
6. F. F. Ehrich/B. H. Perkins/Newark Library
7. P. J. Monahan - Newark (Vital Records)
8. E. L. Rodowskas/R. M. Salemi/J. D. Lojewski
9. F. L. Reig
10. R. H. Wetzel/J. W. Minnich/W. A. West
11. J. F. Maurer
12. Newport Colors Research File (M. C. Crossan)
13. Extra
14. Extra
15. Extra
16. Extra
17. Extra

NEWPORT PLANT

PIGMENT COLORS RESEARCH REPORT

SUBJECT: CONTINUOUS CPC SYNTHESIS

PERIOD COVERED: OCTOBER, 1968 - SEPTEMBER, 1969

SUBMITTED BY: F. L. REIG DATE SUBMITTED: 9/11/69

APPROVED BY: J. F. MAURER J. F. Maurer

ABSTRACT

Continuous formation of a stable intermediate isoindolenine can easily be formed in a pipe line "flow" reactor. Synthesis of CPC from the intermediate could be accomplished in a cascade or staged reactor. Benefits of CPC quality uniformity and simplicity of processing would be realized in such a synthesis system.

TABLE OF CONTENTS

KN-69-12
Newport, Delaware

I. INTRODUCTION

The phthalic anhydride-urea process is used to make the major portion of copper phthalocyanine in this country. DuPont Pigments has used the process with a purified kerosene carrier since the conception of CPC manufacture at Newport in 1948. Some countries use phthalonitrile because of better yields and simplified processing but this raw material cannot be justified economically in the United States because of the low cost of phthalic anhydride and urea.

E. F. Klenke suggested that a possible area of cost reduction might be realized in a semi-continuous process for making crude CPC over the batch process being used at Newport (Reference 1).

Early semi-works acid flushings of the crude CPC synthesis mass indicated potential quality problems due to the margin of difference in impurity levels from batch CPC synthesis. In addition, since both flushing and HT drowning were visualized as "flow" reactions, it seemed that additional benefits other than uniformity of quality might be realized by "flow" synthesis route (Reference 2).

Search of the literature indicates that intermediate isoindolenines in the route to CPC were highly stable compounds and could be produced in a "flow" reactor (Reference 3).

Reference 1 - EFKlenke to JHCooper, "CPC Cost Reduction", 4/27/60

Reference 2 - Reig "Flow Reactor Concepts", NB-3244-17ff, 3/25/69; Engineering Computation Sheets 1 and 2, 11/19/68

Reference 3 - "Isoindolenines", Angewandte Chemie 68, pp. 133-150, 1956

II. CONCLUSIONS

The continuous formation of stable intermediate isoindolenines can easily be formed in a pipe line "flow" reactor. Benefits of uniformity of quality and simplicity of processing would be realized. The final formation of CPC would be difficult in a "flow" reactor but would present no problems in a cascade or staged stirred reactor system being fed by the intermediate unit and being discharged by gravity flow or an open centrifugal pump.

III. ACKNOWLEDGEMENT

Considerable guidance in the pursuit of this process concept in the laboratory was obtained from E. F. Klenke and J. W. Minnich. R. H. Wetzel offered several suggestions for equipment simplification.

IV. DISCUSSION

The initial work was carried out in the standard two liter CPC synthesis flask using normal plant concentrations for kerosene, phthalic anhydride, urea, copper chloride, DBPC anti-oxidant and ammonium molybdate catalyst. The amounts were:

68 g	PA
95 g	Urea
11.6 g	$CuCl_2$
.22 g	DBPC
.325 g	AMM
450 ml	Deobase Kerosene

If the ingredients are charged in the normal fashion and heated to the intermediate stage of reaction (120-135°C.), considerable foaming due to the erratic evolution of CO_2 was noted. It was observed if the ingredients were highly dispersed, that is, high speed mixing in an Oster blender, the evolution of gas at the intermediate reaction stage was more uniform and rapid heat-up could be accomplished without foamover.

A temperature profile is attached.

When this mixture was fed to a 19 mm ID pyrex tube using a glass funnel as a feed reservoir and a flexible Teflon tubing between the funnel and reactor, a continuity of feed could not be established because of plugging. If kerosene in the mix was reduced 30%, the feed required help from a blast rod slightly smaller than the stem of the reservoir funnel but the reactor gave a uniform discharge. The character of the discharge varied with the temperature maintained over the 36 inches length that was heated with Glascol heating tapes, operated in three separate 12 inch sections and controlled by an 0-120 V variac on each section.

At 104-108°C., the intermediate product was a light bluish salt and some free kerosene. At 115-120°, the salt was light green-grayish in appearance with free kerosene. The free

IV. DISCUSSION (Continued)

kerosene in both cases was water white. If the temperature was elevated to 137-140°, a yellowish green product was obtained and the kerosene had a reddish tint. All three intermediate products yielded CPC in good yield when heated as rapidly as possible (20 minutes) from room temperature to 313°C. on a hot-plate in a beaker using a magnetic stirrer bar for agitation (Reference NB-3244-39,40). If the cold well dispersed synthesis ingredient mass was heated in a similar beaker, CPC was not formed but the product was a dark brown mass with considerable phthalimide.

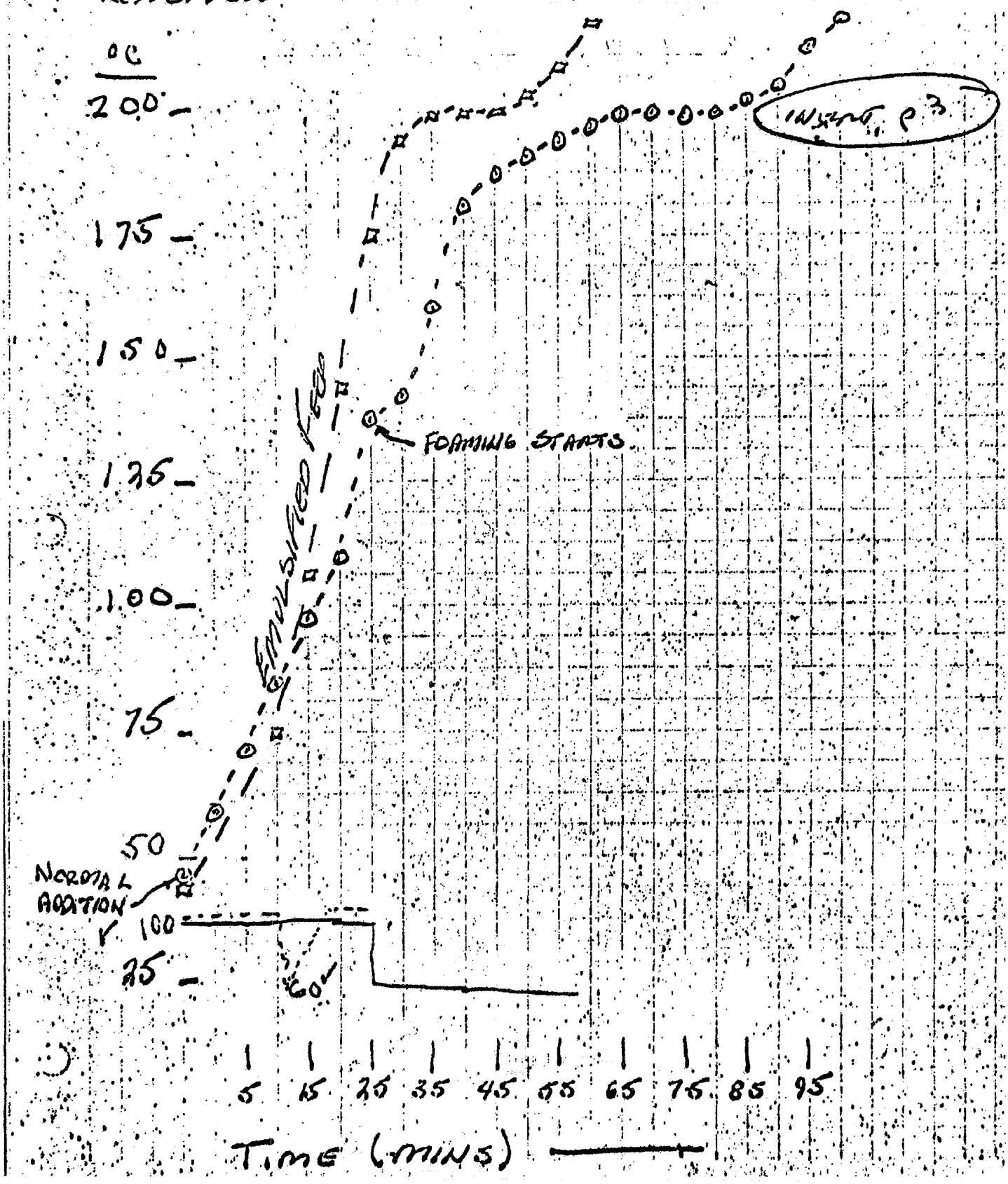
A 3 liter Hastelloy C-276 reactor was converted into a 3-staged reactor unit with a continuous feed pump and a method for discharging the reactor continuously (see Attachment #4). The initial run failed to yield useful rate data because of pluggage in the heat exchanger on the feed side shortly before start-up. Attempts to bypass the heat exchanger were unsuccessful but analyses of material from the top and bottom stages of the reactor indicated all the feed (2400 grams) had converted to CPC. The heat exchanger was redesigned and several subsequent runs of two and 3-1/2 hours were successful. (Ref: NB-3243-10-15).

Using the 3.64MM lbs./yr. Blue required for the October, 1968, CPC market potential would indicate a 500 lb./hr. unit at 85% utilization, that is, a 500 gallon reactor system (see Attachment #2).

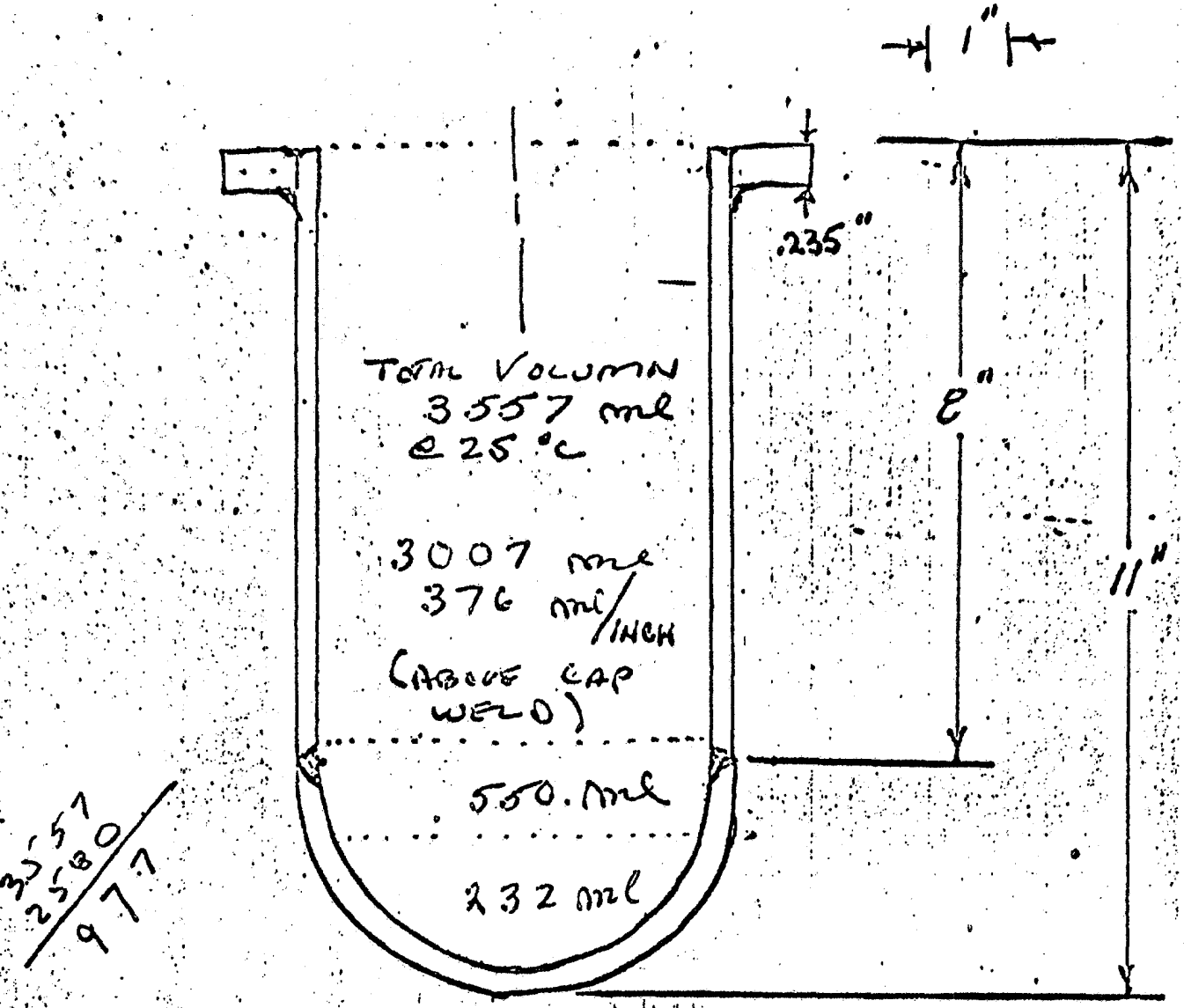
V. ATTACHMENTS

1. Hastelloy C-276 Laboratory Reactor
2. Flow Reactor Concepts, 11/19/68
3. Pre-Start-up Survey - Continuous CPC Synthesis, 3/17/69
4. Flow Reactor Lab Unit, 3/25/69
5. Postulated CPC Synthesis, 4/24/69

EMULSIFIED FEED 372
L C SYNTHESIS NEWPT.
REACTION RATE FLR DATE 12-9-60

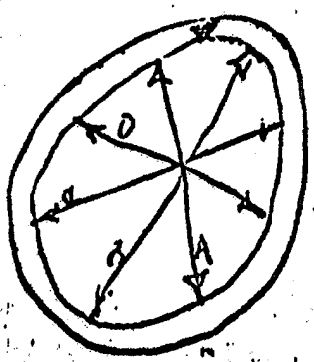


CPC SYNTHESIS 322
HASTELLOY C-276 NEWP
LAB REACTOR FLR 12 - 11 - 6



3257
2580
977

WT MT - 13.5 LBS
6129 g



D.A
A - 5.0E
B - 5.10
C - 5.07
D - 5.05

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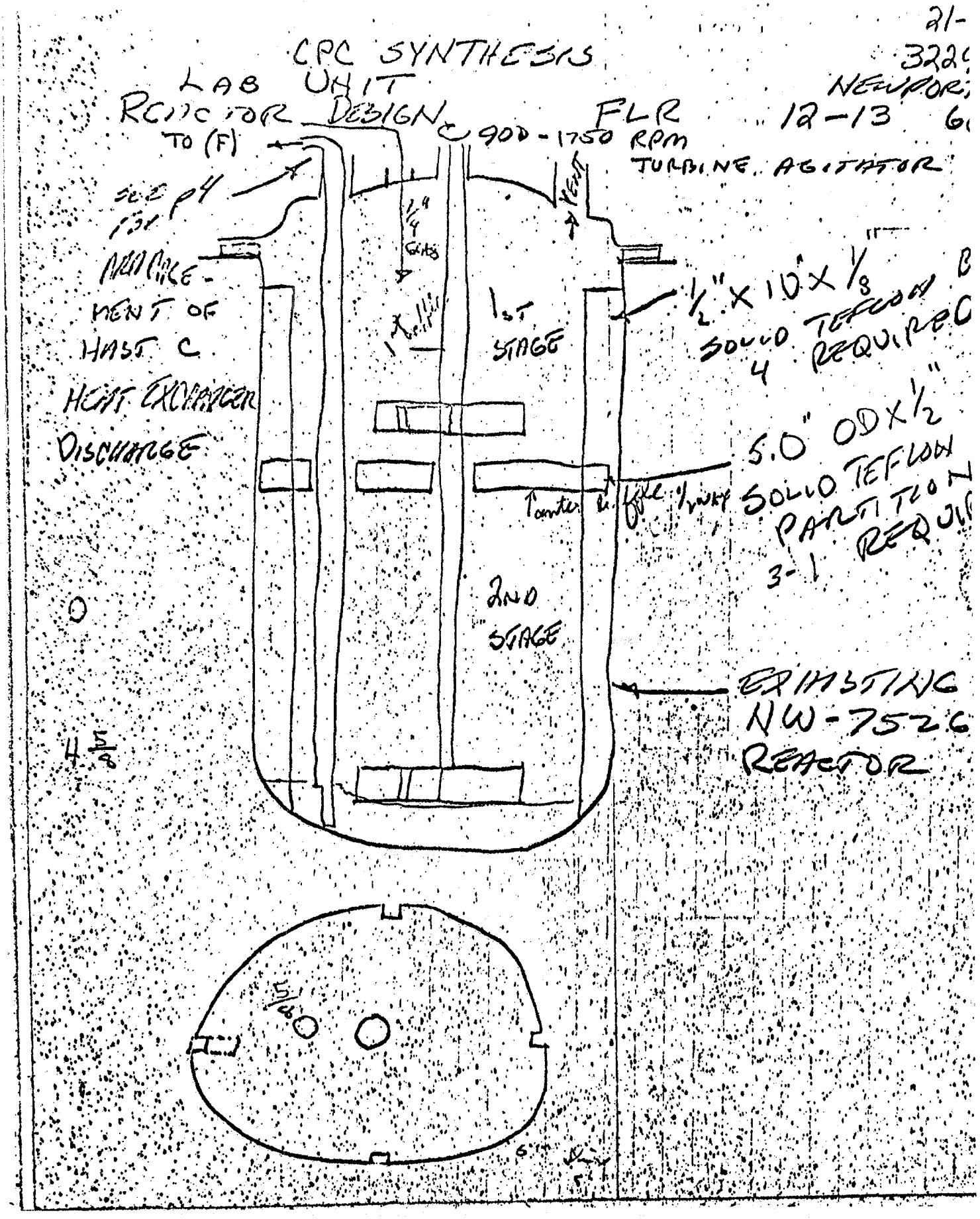


CPC MANUFACTURE 41-45
CONTINUOUS SYNTHESIS, HT NEWPORT
PENNINE FIE 10-2-68

REPLACE PRESENT BATCH PROCESS
CONT SYNTHESIS

ADVANTAGES	DISADVANTAGES
UNIFORM QUALITY	NEW INVESTMENT
HT DROWN	
IMPROVE YIELDS	HIGHER H_2SO_4 COST
ie KEROSENE	NEEDLES PURIFICATION
CPC	ie LC/GREEN
HIGHER PURITY	LC/BGD
UNIFORM QUALITY	
ELIMINATE DRYING	
ie BR	
BBF	
BBX	
ELIMINATE DRY MILLING	

HIGH SPOT COSTS @ 256 M#/MO (AUG 68)
9 PHASE PRODUCTS

INCREASES	M$/MO
SYNTHESIS INVEST	5.00
ACID (2X4.4)	8.80
WASTE DISPOSAL	5.00
	18.80

SAVINGS	
KERO (½ 8.48)	4.24
YIELD (.02)(256)(1.54)	7.90
NO DRY MILL (147)(.06)	8.82
NO NaOH (TO NEUTR)	5.00
NO DRYING (BR, BBX, BWF) 73(.05)	3.65
	29.61
NET SAVINGS (29.61 - 18.80)	10.81
APPOX	120/YR

CPC MANUFACTURE (CONT)
CONTINUOUS SYN, HTD, EXT — WHERE NEWPORT
FLR — DATE 10-2 — 69

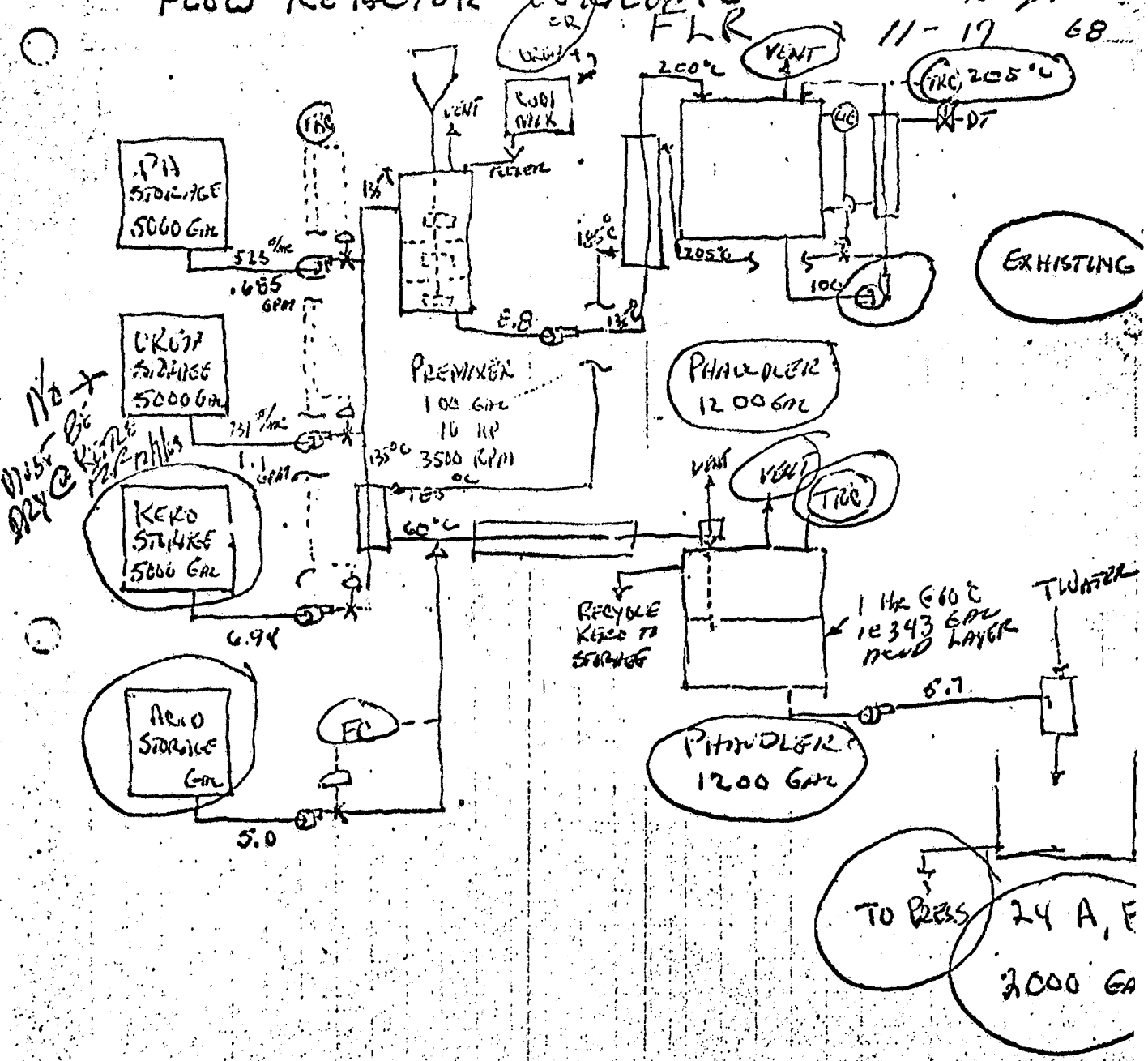
HIGH SPOT COSTS (CONT)
LC FOR BGD, BGS, GRY

	M $/MO
INCREASES	
SYN / INVEST	1.50
ACID	3.08
	4.58
SAVINGS	
KERO	1.70
YIELD	1.44
	3.14
NET COST (4.58-3.14)	1.44
APPOX	17/YR
TOTAL NET SAVINGS APPOX	103/YR

41-450

CONTINUOUS CPC SYNTHESIS FLOW REACTOR CONCEPTS

FLR 11-17 68



CONT SYNTHESIS - MARKET 47.3% 41-45U
POTENTIAL FLR NEWPT 11-19-68

MARKET POTENTIAL (1974)

GREEN 1.56 .78 (BLUE REQ'D)

BLUE 2.86

3.64

3.64 / .85 UTILIZATION = 4.3 DESIGN RATE

4.3 MM / 365 x 24 = 500 LBS/HR

SYNTHESIS MASS = 528 GALS/HR
@ 25.6 YLD (LC) = 8.8 GPM

PA 148 MWF = 500 136/130 = 523 LBS/HR
= 41 GPH
= .685 GPM

UREA 60 MWF = 500 190/130 = 731 LBS/HR
= 66 GPH
= 1.1 GPM

CuCl/DBPC/AM = 500 (23.1 + .5 + .65)/130 = 93.5 LBS/HR (23.1 / 1.15 / 24.25)
= 1.56 LBS/MIN

KERO = 500 900(#D)/130 (8.53 (TBD)) = 41.6 GPH
6.94 GPM

JLR

FLOW REACTOR CONCEPTS
REACTIONS RATES
LC SYNTHESIS

2-28-69
3244-B

A. $\frac{1325}{1500 \times 5.5 \times 60} = .00268$ LBS/GAL/MIN — PLANT GLASS

B. $\frac{.3}{.53 \times 240} = .00236$ LBS/GAL/MIN — LAB GLASS

C. $\frac{.26}{.53 \times 66} = .0086$ " — LAB GLASS (HONEYCOMB)

D $\frac{.1}{.79 \times 1} = .126$ " — EXTRUDED HASTELLOY C. CORE WALL

Newport, Delaware
March 17, 1969

PRE-START-UP SURVEY
CONTINUOUS CPC SYNTHESIS

Location: Building A-21 - Lab 307 - 3rd Floor

Personnel Responsible: F. L. Reig, Chemical Engineer
Paul A. Rogers, Technical Assistant

F. L. Reig 3/17/69

I. Operation to be Performed

A. Continuous synthesis of CPC by feeding a pre-mixed slurry at 45°C through a glass lined heat exchanger to a 3-stage reactor which will be held at 200°C operating temperature.

B. Pressure of the unit is atmospheric except 5# psi maximum across the glass lined heat exchanger.

Temperature is 45°C inlet - 200°C reactor and 150°C product discharge.

C. See sketch attached. Diagram.

D. Initial syntheses (batch wise) have been completed in the 3 l Hastelloy "C" reactor.

II. Equipment

The equipment involved are:

A. Hastelloy "C" feed pump with Teflon and carbon impeller.

B. Glass lined heat exchanger. 1/4" nominal OD feed pipe and 1/2" nominal OD product jacket.

C. Three l Hastelloy "C" staged reactor with 4 baffles and two turbine blades turned at 900 rpm by a compressed air turbine.

D. Product pump - Same as feed pump but connected to a variable speed drive to maintain constant level in the reactor.

III. Service Facilities

Compressed air for the reactor agitator, 110V outlets for feed and product pumps and the heavy duty heating jacket on the reactor.

IV. Hazards

A. Chemical

Kerosene at 200°C constitutes the major hazard.

B. Electrical

All electrical equipment has been grounded and have pull-out plugs for lockout procedure.

C. Physical

The glass heat exchanger (broken glass) and agitator speed (900 rpm) constitute the greatest physical hazards of the unit.

V. Safeguards

The equipment is housed completely in the walk-in ventilation hood. Adequate exits, stairwells, etc., are provided for Lab 307. Fire extinguisher is located immediately adjacent to the north door.

VI. Protective Equipment

A. Normal Operation

Safety goggles and safety shoes.

B. Stand-by Equipment

Safety shower located adjacent to hood. Fire extinguisher as noted in V.

FLR:mc

DISTRIBUTION(Include)

1. Area Engr. W.E. Stuefer/W.H.Chambers
2. Prod. or Res. Personnel J.W. Minnich/G. Grimm
3. Plant or Lab. Engineer F. L. Reig
4. S&F Supv. ~~L.H. Wood/D.F. Reddish~~

FORM: #1094
New: 2/8/66

DATE: 3/18/69

PRE-STARTUP SURVEY
~~EQUIPMENT SAFETY ACCEPTANCE~~
PROJECT NO.:
NEWPORT PLANT

EQUIPMENT: Continuous CPC Synthesis

F.A. NO. None BLDG. NAME & NO. A-21 - Lab 307 3rd Floor

The above building-and/or equipment has been inspected and found acceptable with the following exceptions:

1. Fabricate a plastic shield for operator protection in case of glass heat exchanger breakage. - Complete 3/26/69 DFR
2. Locate operating switch for feed and product pumps outside the walk-in hood (JWM suggestion). Complete 3/26/69
5.
6.
7.
8.
9.
10.
11.
12.

ACCEPTANCE COMMITTEE

Dept. Supvn./ Chems., Engrs. G.Grimm ✓ GG
W.L. Monson WLM
F.L. Reig F.L.R.

Plant Eng. or Res. Mechanical ~~W.E. Stuefer~~ ~~W. H. Chambers~~ Did not attend Charles Harrington

Others: Paul A. Rogers PAR

S&F Supvr: L.H. Wood/D.F. Reddish DFR Approval:

Dept. Head or Res. Mgr. J. W. Minnich Date:

TO BE USED ONLY WHERE MINOR OR NO CHANGES IN OPERATING PROCEDURES OR EQUIPMENT DESIGN ARE INVOLVED. ALL OTHERS REQUIRE STANDARD PRE-START-UP SURVEY.

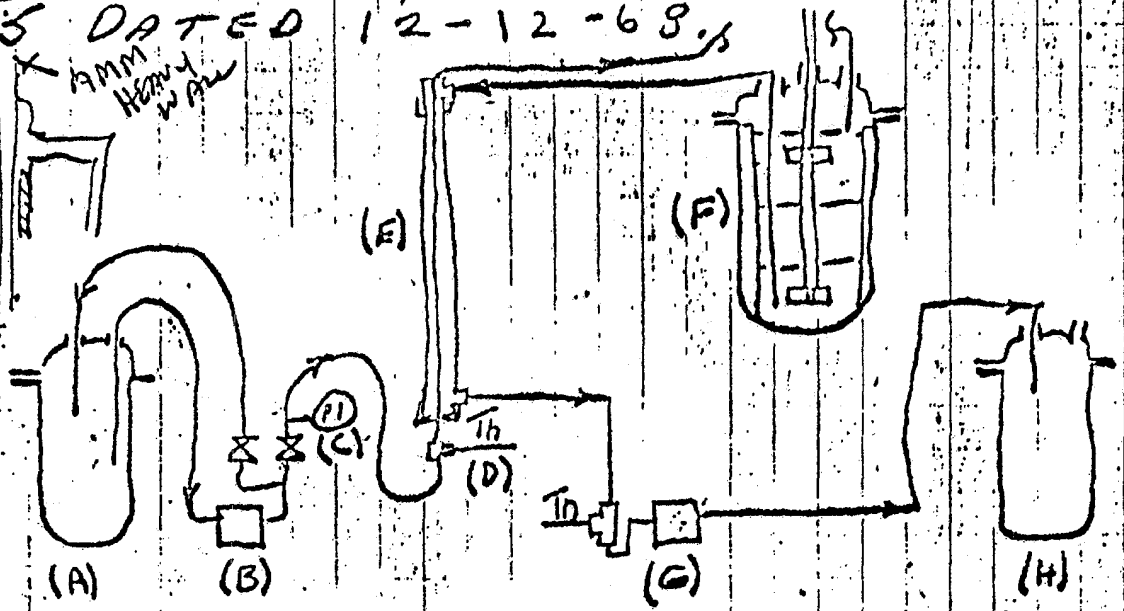
ENGINEERING COMPUTATION SHEET — Sheet No. 1

Title: CONTINUOUS SYNTHESIS — Project No. 41-450

Subject: CPC - CONT. SYNTHESIS — Made by: NEWPT — Work No. 3244-17

O — 307 LAB UNIT — Checked by: FLR — 3-25-69

SEE PB AND NB3229-1,2,3,6,8,16,17,18,19,21 FOR INITIAL WORK THAT LED TO THE DESIGN OF THIS CONTINUOUS CPC SYNTHESIS UNIT. SEE ALSO PRELIMINARY ENGINEERING COMPUTATION SHEETS STUDY NO 3229-21 PAGES 1 TO 5 DATED 12-12-68.



A) 2 l RESIN FLASK, FEED
B) ECO HAST C FEED PUMP
C) FEED CONTROL, 1/4" NEEDLE VALVE, 0-60" H_2O PRESSURE GAGE.
D) FEED TEMP (0-150°C)
E) GLASS HEAT EXCHANGER 1/4" (6MM) FEED TO REACTOR, 1/2" (13MM) PRODUCT RETURN
F) 3 l HASTELLOY C-276 REACTOR SEE P 13 FOR DETAIL, PRODUCT TEMP (100-300°C) @ 2ND STAGE GC PUMP
G) ECO HAST C PRODUCT PUMP, VARIABLE SPEED DRIVE.
H) 2 l RESIN FLASK, PRODUCT RECIEVER

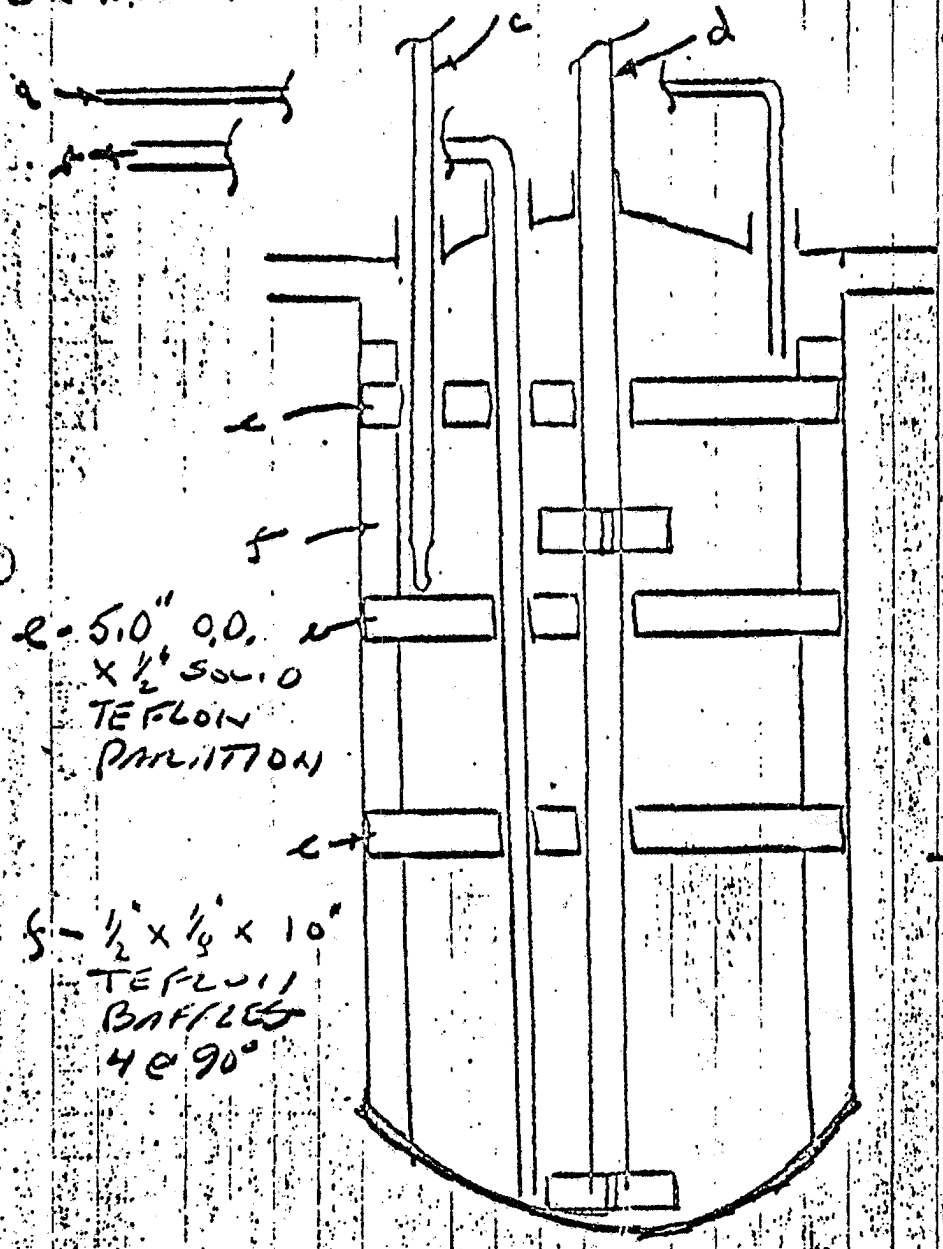
CON'T P 19

11-458

CPC - CONT SYNTHESIS NEWPT 3244-13

HASTELLOY C-276 REACTOR FLR 3-25-69

SEE NB3229-17 FOR MEASUREMENT & WEIGHT OF THIS VESSEL AS RCCD ON 1.2-12-68 WHEN PURCHASED (NW-7526)



a - 6 MM GLASS FEED INLET

b - 13 MM GLASS PRODUCT OUT

c - 0-300°C TH

d - 900 RPM TURBINE AGITATOR

e - 5.0" O.D. X ½" SOLID TEFLON PARTITION

f - ½" X ⅛" X 10" TEFLON BAFFLES 4 @ 90°

TOTAL VOLUME 3500 ml

375 ml/INCH

Proj. or Serial No. 41-450

Subject CPC - CONT. SYNTHESIS — Author NEWPT — W.O. No. 3244-19

SYNTHESIS CHARGE — File FLR — 3-26-69

CHARGE TO REACTOR:

3 l LC 1906 SYNTHESIS SLURRY (1.0 LB CPC / 3780 ml)

360 g CPC CONTENT

CHARGE TO FEED FLASK

204 g PA

1350 ml KERO

MIX 1 MIN OR TIL UNIFORM

285 g UREA " "

34.7 g $CuCl_2$ " "

.75 g DPBC " "

.925 g AMM MOLY " "

HEAT REACTOR TO 200°C ± 5°C

ADJUST FEED TO REACTOR TO 300 g PER MIN AND PRODUCT REMOVAL TO 300-350 g PER MIN

CONTINUE TO CONTROL REACTOR TEMP @ 200°C ± 5°C AND RECORD EVERY 15 MINS:

FEED FLASK WT g

" °C

FEED TO REACTOR WT

INLET HE °C

REACTOR °C

ROTATOR RPM

LEVEL

CONT. P. 19

41-450

CPC - CONT SYNTHESIS NEW# 3244-20

SYNTHESIS CHARGE FOR 3-26-69

RECORD QUERY IS MWS, CON'T

PRODUCT WT
OUTLET IIE
% CPC
% KERO

RECHARGE FEED FLASK AS REQUIRED USING THE OSTER BLENDER TO OBTAIN UNIFORMITY BEFORE CHARGING. P CONTENT WEIGHT IS 1/3 THE ORIGINAL CHARGE, IE:

78	g	PA
450	gms	KERO
95		UREA
11.6	g	$CuCl_2$
.125	g	DPBC
325	g	PARA MOLY.

1) FOR % CPC 10 g PRODUCT
90 g H_2SO_4 CONC
HEAT TO 60°C WITH AGITATION
TRANSFER TO 150 ml GRAD SEP FUNNEL
SETTLE 30 MINS
DROWN 50 g LOWER (ACID) LAYER IN 1 l WATER
FILTER, WASH SOLIDS TWICE
DRY WT X = % CPC

FOR % KERO MEASURE UPPER LAYER
ml X .8 X 10 = % KERO

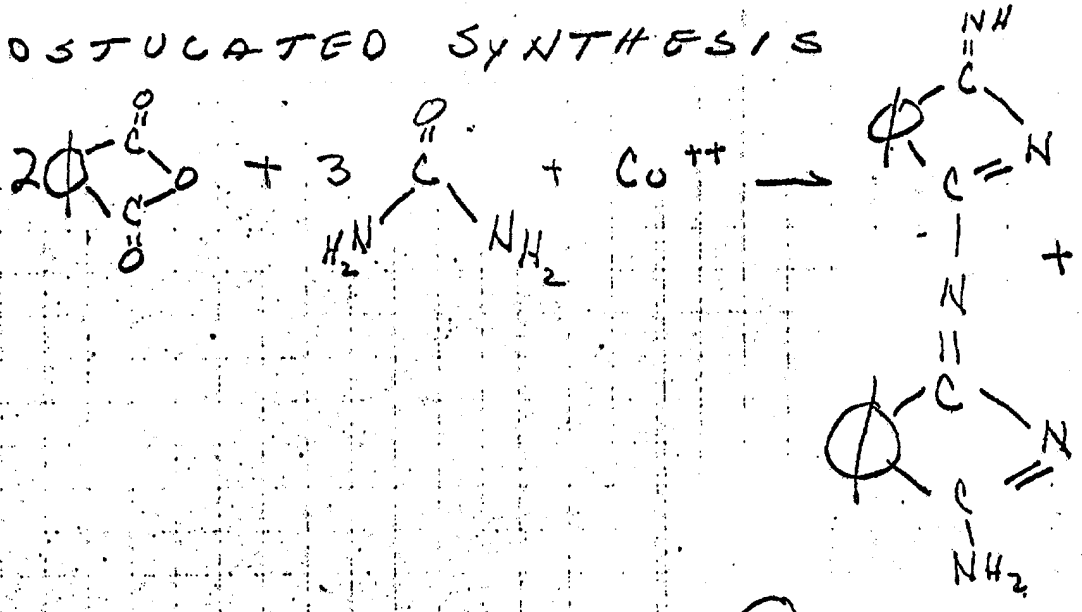
CONTINUOUS CPC SYNTHESIS — 41-450
POSTULATED SYNTHESIS — NEWPORT
VIA ISOINDOLENINE — FLR — 4-24-69

4 PA + 14.5 U + $CuCl_2$ → CPC + NH_3 + CO_2

WT 1.0 1.5 .25 1.0 .73 .83

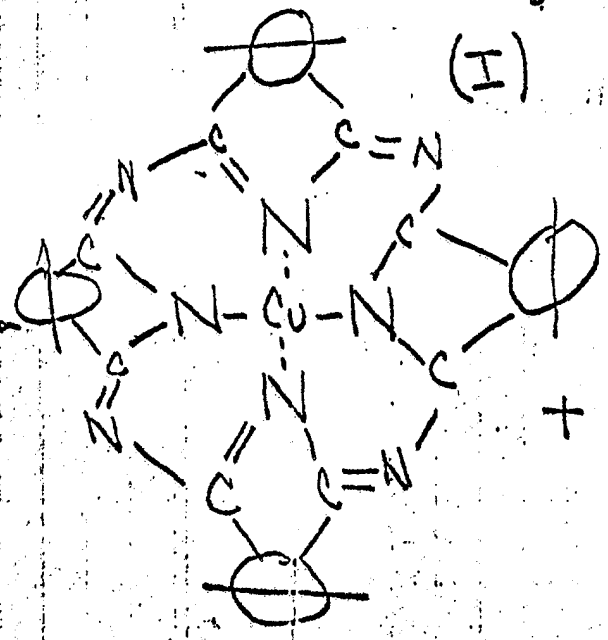
+ H_2C
+ HCl
$(NH_4Cl$

POSTULATED SYNTHESIS



+ $3CO_2$
+ NH_4Cl
+ $3H_2$
+ H
+ H_2
+ Cu^{++}

(I)



+ NH_3

(++)

CPC SYNTHESIS (CONT) Proj. 41-460

CURRENT STEPWISE Work NEWPORT

SYNTHESIS Comp. FLR Date 4-24 19 69