KN-69-19 4,11-DICHLORO DAA TFA PROCESS By: R. A. Johnson 10/68 - 9/69

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NEWPORT PLANT

PIGMENT COLORS RESEARCH REPORT

SUBJECT: 4,11-DICHLOR DQA TFA PROCESS

PERIOD COVERED: OCTOBER, 1968 - SEPTEMBER, 1969

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SUBJECT: 4,11-DICHLOR DQA TFA PROCESS

PERIOD COVERED: OCTOBER, 1968 - SEPTEMBER, 1969

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SUBMITTED BY: R. A. JOHNSON RAJ DATE SUBMITTED: 10/1/69

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ABSTRACT

A TFA process, using the N-methylaniline salt as condensation catalyst, has been developed for making 4,11-Cl_2DQA. The unfavorable equilibrium controlling the condensation was overcome to give good yields. Tar formation has been minimized.

TABLE OF CONTENTS

I. INTRODUCTION AND OBJECTIVES

Production is currently using a PTSA process for making 4,11-Cl_2DQA. This process appears limited to a 108% concentration. At higher concentrations, both yield and fluorescence drops off. Even at the 108% concentration, yields are less than optimum. These yield losses contribute to the tar problem. It was the object of this study to develop a workable TFA process which would operate at increased batch concentrations, would increase yield, and would produce less tars.

II. SUMMARY AND CONCLUSIONS

1. A TFA process was developed for making 4,11-Cl_2DQA at a 216% batch concentration. Further increases in batch concentration should be possible.

2. The condensation step is controlled by an unfavorable equilibrium. Water removal is the key to maximizing yield.

3. Increased condensation temperature is the least effective means of increasing yield, since it is limited by the volatility and/or dissociation of the catalyst.

4. The vapor pressure of water can be reduced to increase the condensation yield by lowering pressure either alone or in combination with a nitrogen sweep.

5. Conditions which are effective for reducing the vapor pressure of water also remove the self catalyst, the o-chloranilinium salt of TFA. This can be minimized by using a less volatile catalyst such as the N-methylanilinium salt of TFA.

6. The use of the N-methylanilinium salt of TFA as catalyst should eliminate plugging during its removal by distillation, since it is a liquid (MP 26-7°C.) under these conditions.

7. The anilinium salt is the catalyst in the condensation reaction. It polarizes the carbonyl groups on SSE to form carbonium ions which can then react with OCA.

8. 2,2'-Cl_2DAT in DT shows evidence of thermal degradation at 150-5°C. This can be largely prevented by holding and transferring to pyrolysis at 120-5°C.

III. PATENT STATUS

The use of TFA is covered by 1572-K (allowed 10/18/67). A patent proposal is being prepared on the use of N-methylaniline as a catalyst.

IV. SUGGESTIONS FOR FUTURE WORK

1. Modify plant jets to increase capacity so that a nitrogen sweep can be used.

2. Increase batch size beyond 216% concentration.

V. DISCUSSION OF RESULTS

Results will be discussed in the order in which they occur in the synthesis.

A. SSE

No work was done on SSE. This is a well established process developed in the unsubstituted quinacridone studies.

B. Condensation

1. o-Chloraniline

The use of stoichiometric amounts of OCA and SSE resulted in a low yield of 2,2'-Cl_2DAT. Increasing the mole ratio of OCA:SSE to 4.5:1 gave yields in excess of 90% of theory as Cl_2DQA. No further increases in yield were obtained by increasing the mole ratio beyond 5.5:1 (see Table I). This data was obtained at 80-90°C./50 mm Hg and using the o-chloranilinium salt of TFA as catalyst.

TABLE I

Effect of OCA:SSE Ratio in the Condensation on Yield
Condensation temperature = 80-90°C.
Condensation pressure = 50 mm Hg

OCA:SSE	Yield (as Cl_2DQA)
3.0:1	78.6%
3.5:1	86.6%
4.0:1	89.0%
4.5:1	91.3%
5.0:1	91.2%
5.5:1	92.9%
6.0:1	92.8%

V. DISCUSSION (Continued)

B. Condensation (Continued)

2. Catalyst

Varying the concentration of TFA between the equivalence of 10 pounds/batch up to 40 pounds/batch had only a slight effect on yield. This experiment was run at 80-90°C./50 mm Hg, OCA:SSE of 5.5:1 and a 2-hour hold.

TABLE II

TFA Concentration	Yield as Cl_2DQA
10#	90%
20#	90%
30#	92%
40#	93%

The results in Table II are estimated to be accurate to ±1%. Hence, the OCA-SSE condensation reaction does not appear to be rate controlled.

The amine associated with TFA determines the effectiveness of the catalyst. TFA is a proton doner, while the resulting anilinium ion polarizes the carbonyl groups on SSE. The resulting carbonium ion can then react with OCA to form Cl_2DAT. The use of a more basic amine such as N-methylaniline, as the catalyst, increased the rate of the reaction but did not increase the optimum yield. Again, evidence that the reaction is equilibrium controlled.

TABLE III

OCA:SSE	Yield at Cl_2DQA OCA·TFA	NMA·TFA
2.05:1	39%	65%
2.50:1	43%	72%
5.50:1	95%	92%

V. DISCUSSION (Continued)

B. Condensation (Continued)

3. Time

During the first hour of the condensation at 80-90°C./25 mm Hg, yield increased rapidly with time. (See Figure 1.) Water removal now became limiting, since the concentration of water was within the solubility limits of the OCA-DT system. After 2 hours, there was no further increase in yield.

4. Pressure

Water removal is limiting in the condensation reaction. Its removal from solution depends on vapor pressure and rate of diffusion. The vapor pressure can be reduced by reducing the total pressure on the system. This was demonstrated by condensations run at 80-90°C. At 50 mm of Hg, the yield as Cl_2DQA was 92% of theory while at 25 mm of Hg, it was increased to 95% of theory. Since the yields could not be increased by running the reaction for a longer period of time, this is a static effect.

The initial attempt to obtain a further increase in yield by decreasing the pressure to 10 mm Hg was unsuccessful. This was found to result from a loss of the OCA·TFA catalyst. By using the N-methylaniline salt of TFA, a less volatile catalyst, it was possible to run the reaction at 10 mm Hg. The following data further substantiates the effect of reduced condensation pressure on yield:

Pressure	Temperature	Yield (SSE to Cl_2DQA)
50 mm Hg	95°C.	93.6%
10 mm Hg	95°C.	99.6%

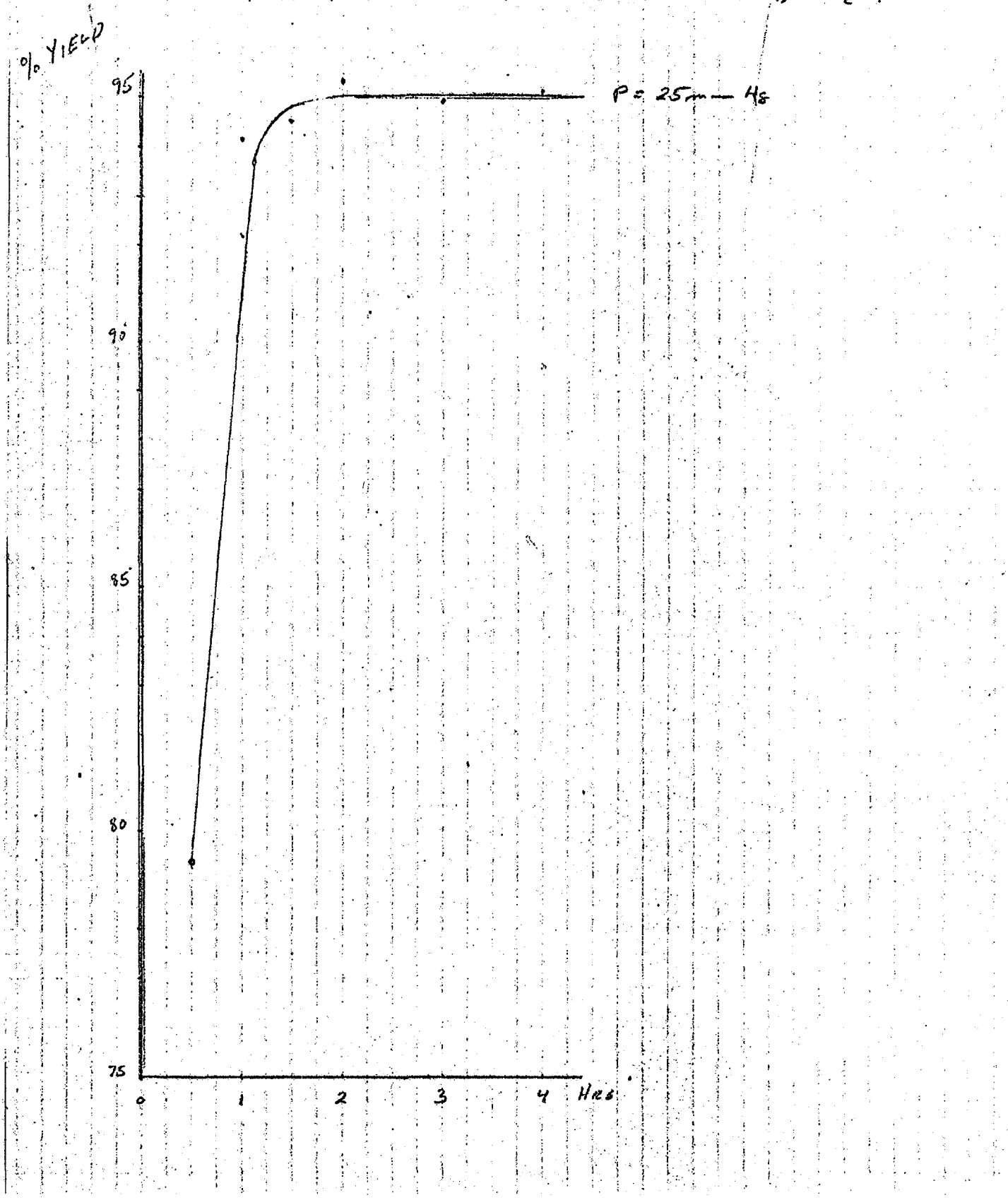
Based on these results, the reaction is equilibrium controlled.

5. Nitrogen Sweep

Reducing pressure to increase yield is a static approach, since increasing the hold time beyond

FIG. 1

HOLD TIME AT 80-90°C VS. YIELD AB 4,11-Cl_2DQA



V. DISCUSSION (Continued)

B. Condensation (Continued)

5. Nitrogen Sweep (Continued)

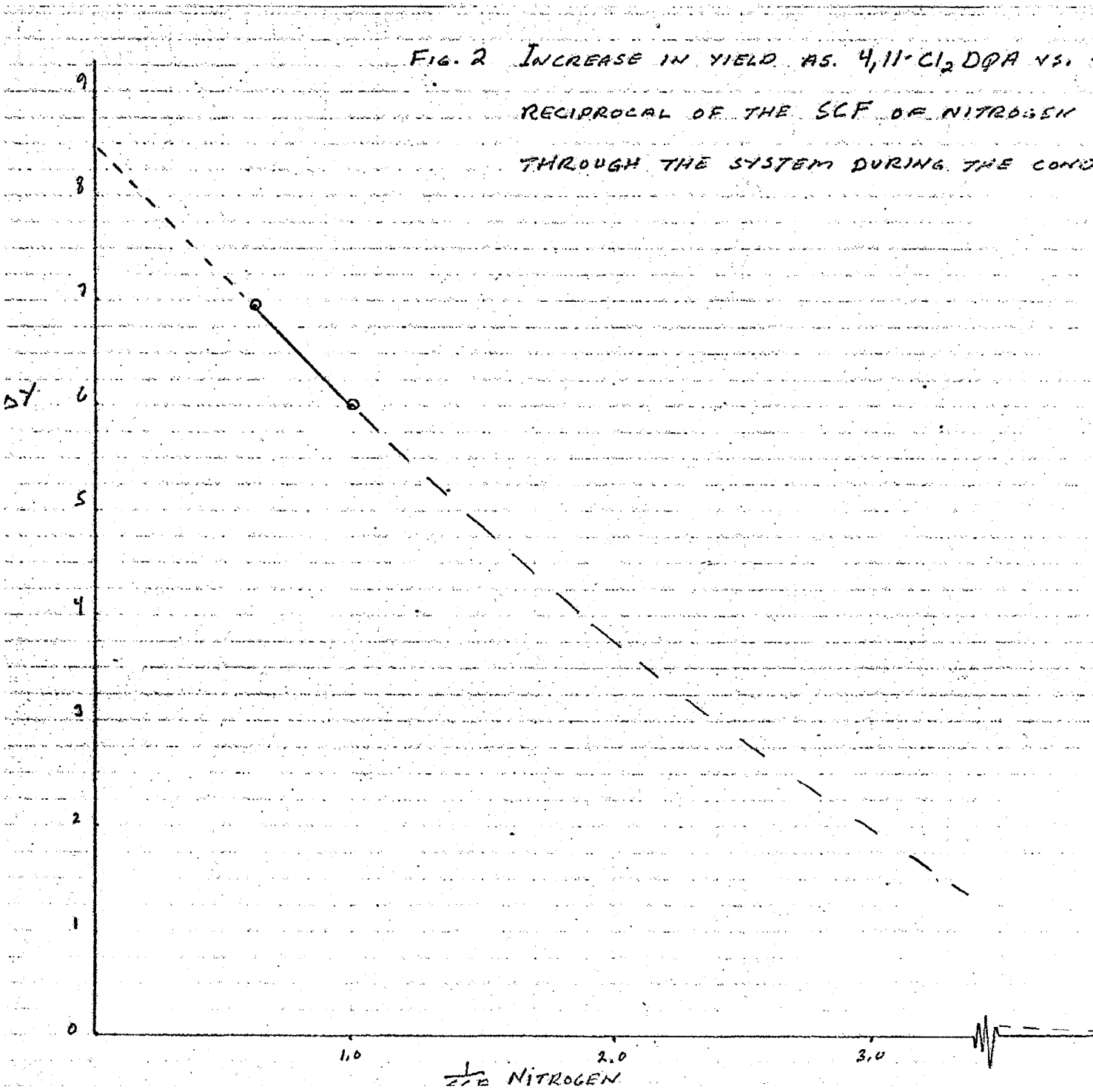
two hours gave no further increase in yield. A dynamic method of reducing the vapor pressure of water as well as increasing the diffusion rate is the use of a nitrogen sweep. Initial studies were run at a pressure of 25 mm Hg and 50 mm Hg respectively and a temperature of 80-90°C. In both cases, yields were less than when no sweep was used. This again points out the volatility of the OCA salt of TFA.

The catalyst volatility problem was again minimized by using the NMA salt in place of the OCA salt of TFA. Temperature and pressure were 80-90°C. at 50 mm Hg. Nitrogen flows for two runs were 0.5 SCFH and 0.8 SCFH, respectively. These gave Cl_2DQA yields from SSE of 96.4% and 97.3%. Under these same conditions, at 0.0 SCFH, the yield was only 90.4%. Figure 2 is a plot of the increase in yield as Cl_2DQA vs. the reciprocal of the SCF of nitrogen put through the system during the condensation. Extrapolation to zero water vapor pressure indicates that the maximum yield for the combined condensation and pyrolysis is 99% of theory. To use either the static or the dynamic methods of reducing water vapor pressure to increase yield in the plant will require increasing the capacity of the vacuum jets.

6. Temperature

Yield, as Cl_2DQA, increases with increasing condensation temperature up to a point. Above this temperature, yields decrease. The point of maximum yield is determined by the catalyst used. For OCA·TFA, this occurs between 80°C. and 90°C., while for NMA·TFA, it is very close to 95°C. The greater volatility of OCA·TFA was shown by the following TGA results:

Catalyst Salt	Start to Lose Wt.	Wt. Loss at 100°C.
OCA·TFA	60°C.	30%
NMA·TFA	80°C.	8%



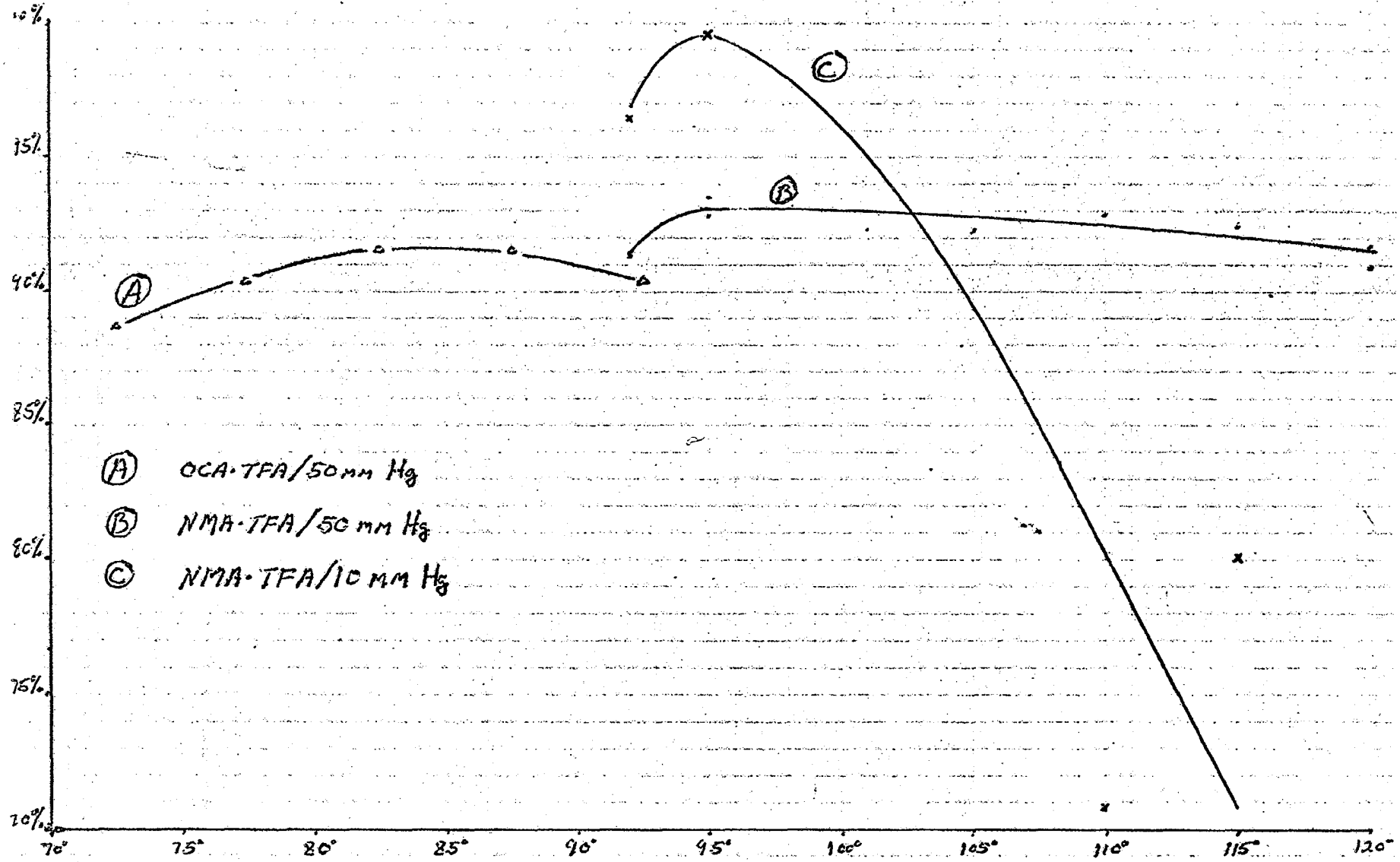


FIG. 3. YIELD OF 4,11-Cl_2 DQA FROM SSE VS. CONDENSATION TEMPERATURE

V. DISCUSSION (Continued)

B. Condensation (Continued)

6. Temperature (Continued)

Hence, the maximum yield to be obtained by increasing the condensation temperature is limited by catalyst volatility. Additional evidence for this is that yields decrease with decreasing total pressure above the critical temperature.

7. Equilibrium Constant

The prior results indicate that the equilibrium is controlling yield. Since the equilibrium appeared to be unfavorable, a study was made to determine the equilibrium constant. The condensation is a two-step reaction:

$$SSE + OCA \rightleftharpoons ClMAT + H_2O$$

$$ClMAT + OCA \rightleftharpoons Cl_2DAT + H_2O$$

The overall equilibrium constant is then

$$k_c = k_{c_1} k_{c_2} = \frac{C_{Cl_2DAT}\ C^2_{H_2O}}{C_{SSE}\ C^2_{OCA}}$$

The preliminary calculations were made from data obtained from running the reaction in refluxing 2B alcohol. Similar runs were made for DAT and Me_2DAT for comparison. Since the results were based on product yield, the equilibrium constants were considered to be approximate values for the overall condensation reaction

Product	k_c
2,2'-Cl_2DAT	0.06
DAT	11
Me_2DAT	78

An assumption was made in calculating these values that only 10% of the product was in solution. These results indicate that all three condensations are probably equilibrium controlled and the 2,2'-Cl_2DAT equilibrium is particularly unfavorable.

Table of Calculations

a. In alcohol

		Cl_2 DAT	DAT	Me_2 DAT
(1)	SSE (initial)	0.492 moles	1.260 moles	1.260 moles
(2)	Amine (initial)	2.951 "	3.781 "	3.780 "
(3)	38% HCl	15 ml	32.5 ml	32.5 ml
(4)	Sp. G. 38% HCl	1.1885	1.1885	1.1885
(5)	Wt. of HCl/cc	0.4516 g/cc	0.4516 g/cc	0.4516 g/cc
(6)	H_2O (initial) = (4) - (5)(3) ÷ 18	0.614 moles	1.330 moles	1.330 moles
(7)	Product yield	149.2 g	469.9 g	528.2 g
(8)	" MW	465	396	424
(9)	" # (equilibrium)	0.321 moles	1.187 moles	1.246 moles
(10)	H_2O (equilibrium) = 2(9) + (6)	1.256 moles	3.704 moles	3.822 moles
(11)	SSE (") = (1) - (9)	0.171 moles	0.073 moles	0.014 moles
(12)	Amine (") = (2) - 2(9)	2.309 moles	1.407 moles	1.288 moles
(13)	Product in solution 0.1(9)	0.0321 moles	0.1187 moles	0.1246 moles
(14)	k_c = (13)(10)²/(11)(12)	0.06	11	78

b. In Dowtherm

	Initial	Equilibrium
SSE	0.286 moles	0.286 - 0.256 - 0.025 = 0.005 moles
OCA	1.576 moles	1.576 - 0.537 = 1.039 moles
DT	1.297 moles	1.297 moles
Cl_2 DAT (total)	0.000 moles	219.0 g ÷ 465 = 0.256 moles
Cl_2 DAT (soln.)*	0.000 moles	= 0.110 moles
MET	0.000 moles	0.537 - 2(0.256) = 0.025 moles
H_2O (out of soln.)	0.000 moles	0.537 moles
H_2O (max. in soln.)	0.000 moles	0.035 moles

* Solubility of Cl_2 DAT obtained from Fig. 4. at 88°C.

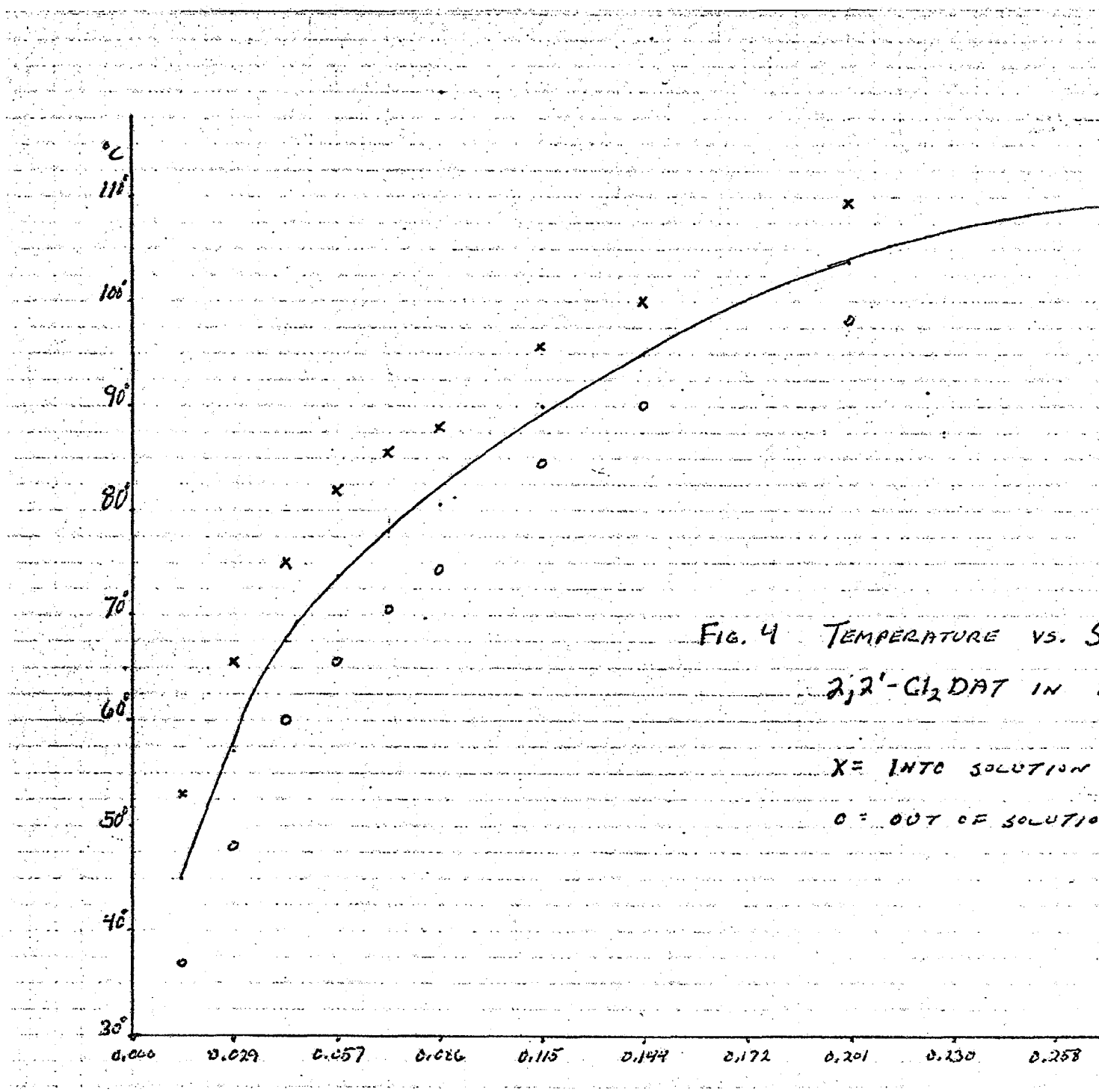


FIG. 4 TEMPERATURE VS. S

2,2'-Cl_2 DAT IN

X = INTO SOLUTION

O = OUT OF SOLUTIO

Water in solution

mole fraction (x) = $\frac{\text{partial pressure (pp)}}{\text{vapor pressure (vp)}}$

25 mm Hg)

DT + OCA at equilibrium (88°C) = 2.336 moles

$pp_{DT} = \frac{1.297}{2.336}(1.0) = 0.6 \text{ mm Hg}$

$pp_{OCA} = \frac{1.039}{2.336}(11.8) = 5.2 \text{ mm Hg}$

$pp_{H_2O} + pp_{N_2} = 25.0 - 0.6 - 5.2 = 19.2 \text{ mm Hg}$

If $pp_{N_2} = 0$, $X_{H_2O} = \frac{19.2}{487} = 0.0394$

$H_2O_{(\ldots)} = \left(0.0394 \times \frac{2.336}{1-0.394}\right) = 0.0957 \text{ moles}$

Maximum possible water from reaction = $(2 \times 0.286) = 0.572$ moles

Then, 0.537 moles < total water < 0.572 moles

Therefore, the maximum water in solution = 0.572 - 0.537 = 0.035 moles

Since this is less than the water calculated from the partial pressure, the partial pressure of nitrogen is not zero.

$pp_{H_2O} \leq \left(\frac{0.035}{0.0957}\right)(19.2) = 7.0 \text{ mm Hg}$

$pp_{N_2} \geq 19.2 - 7.0 = 12.2 \text{ mm Hg}$

Therefore, 0.035 moles is the best value for the water

in solution and will give the maximum value for the equilibrium constant.

$$K_c \leq \frac{(0.110)(0.035)^2}{(0.005)(1.039)^2} = 0.025$$

V. DISCUSSION (Continued)

B. Condensation (Continued)

7. Equilibrium Constant (Continued)

To improve the accuracy of the Cl_2DAT equilibrium constant, the reaction was run in Dowtherm where the solubility of Cl_2DAT and yields of Cl_2DAT and H_2O could be determined. Based on thsse results, the equilibrium constant was equal to or less than 0.025.

C. Pyrolysis

Normal laboratory pyrolysis conditions (KN-67-11) using a Cl_2DAT/DT transfer temperature of 150-5°C. gave good yield (95.9%) and quality. Quality is based on the appearance of the Cl_2DQA and the clarity of the MeOH-DT filtrate. Under laboratory conditions, the Cl_2DAT is held at elevated temperatures for short periods of time in comparison to the plant. To check out the stability of Cl_2DAT in DT, it was held at 150-5°C. for 24 hours prior to pyrolysis. In comparison to the normal minimum hold, the yield decreased 4.6% to 91.3% and the amount of DPU found in the pyrolysis equipment increased. Hence, at 150-5°C., Cl_2DAT degradation takes place. This can be minimized by lowering the Cl_2DAT transfer temperature.

In a similar experiment in which the Cl_2DAT/DT was both held for 24 hours and transferred at 120-5°C., the yield of Cl_2DQA from SSE was 96.4%. Hence, at the lower temperature, little or no degradation takes place.

VI. REFERENCES

Additional data may be found in the following references:

1. Condensation

a. CCA:SSE Ratio

5125-37	4.0:1 to 6.0:1
-42	3.0:1 to 4.5:1

b. Catalyst

5125-39	TFA concentration
-40	" "
-41	Synthesis TFA·OCA salt
-52	" TFA·NMA salt
-53	NMA·TFA
-57	Effect of amine basicity

VI. REFERENCES (Continued)

1. Condensation (Continued)

c. Time

5125-48	30 minutes to 4 hrs. (80-90°C./25 mm Hg)
-56	30 minutes to 4 hrs. (80-90°C./50 mm Hg)

d. Pressure

5125-55	10 mm Hg (TFA·OCA catalyst)
-66	25 mm Hg vs. 50 mm Hg (new lot of SSE)
-72	10 mm Hg (TFA·NMA catalyst)
-81	50 mm Hg "
-88	10 mm Hg "

e. Nitrogen Sweep

5125-60	P = 50 mm Hg (TFA·OCA catalyst)
-61	P = 25 mm Hg (TFA·OCA catalyst)
-68	0.5 SCFM/50 mm Hg/TFA·NMA
-71	0.8 SCFM/50 mm Hg/TFA·NMA

f. Temperature

5125-43	85-140°C.
-44	70-95°C./50 mm Hg
-45	100-10°C./50 mm Hg
-46	70-90°C./25 mm Hg
-79	100-20°C./50 mm Hg/TFA·NMA
-81	95-115°C./50 mm Hg/TFA·NMA
-85	92-120°C./50 mm Hg/TFA·NMA
-88	92-115°C./10 mm Hg/TFA·NMA

g. Equilibrium Constant

5125-58	4,4'-Me_2DAT
-59	DAT
-62	2,2'-Cl_2DAT
-65	Cl_2DAT solubility in OCA/DT
-67	Cl_2DAT solubility in OCA/2B alcohol
-69	Effect of temperature on equilibrium

2. Distillation

5125-63	Effect of 0.05% OCA endpoint
-64	Increase distillate for better OCA removal
-70	Composition of OCA/DT distillation

VI. REFERENCES (Continued)

3. Pyrolysis

5125-51	Pyrolysis of isolated Cl_2DAT
-100	Transfer temperature

4. DPU Formation

5125-49	Slow addition of excess OCA
-54	Cl_2DAT + OCA at elevated temperatures
-73	Hold at temperature prior to adding TFA
-83	Virgin Dowtherm

5. Miscellaneous

5125-47	Cl_2DQA fluorescence
-50	2,2'-Cl_2DAT synthesis and isolation
-74	2,2'-Cl_2DAT standard
-75	Attempted removal of water by benzene azotroph