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NEWPORT PLANT

PIGMENT COLORS RESEARCH REPORT

SUBJECT: PROCESS STUDIES OF THE PYROLYSIS OF DIANILINO TEREPHTHALATE TO DIHYDROQUINACRIDONE

PERIOD COVERED: February--October 1966

DATE: 3/10/67

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PROCESS STUDIES OF THE PYROLYSIS OF DIANILINO TEREPHTHALATE TO DIHYDROQUINACRIDONE

Period Covered: February--October 1966

Submitted By: P. G. Reis
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ABSTRACT

The pyrolysis process was reviewed and correlation was developed relating yield to the process variables. Yield loss was found to be a result of a reaction between by-product alcohol and the dianilino terephthalate or its mono-ring-closed derivative. Some vapor-liquid equilibrium data were obtained on the methanol-Dowtherm and ethanol-Dowtherm systems which showed that these systems form non-ideal solutions. Heat transfer rates to the plant pyrolysis reactor were evaluated.

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STUDY REPORT

PROCESS STUDIES OF THE PYROLYSIS OF DIANILINO TEREPHTHALATE TO DIHYDROQUINACRIDONE

I. INTRODUCTION

In February 1966 an examination of available information on the pyrolysis of dianilino terephthalate (DAT) through a mono-ring-closed intermediate (MRC) to dihydroquinacridone (DQA) was commenced in order to develop basic data for expansion of the existing manufacturing facilities. Although the reaction had been carried out in the laboratory and in the plant for over eight years, the reaction was not well understood and apparent discrepancies existed between laboratory and plant operation. It was the objective of these studies to resolve these discrepancies and, if possible, establish reliable criteria for scale-up.

Several of the unanswered questions and anomalous situations which were apparent were these:

A. Why does increased agitation in the plant increase the yield?

B. Why does the plant consistently operate several degrees above the normal boiling point of Dowtherm A, the reaction medium?

C. Why does it take the plant eight hours to run the reaction, whereas the laboratory can do it in 1-1/2 hours at better yields?

The availability of some unusually good kinetic data on the pyrolysis reaction was of considerable help in resolving some of these questions (KN-66-5, Wesley and Griswold).

II. PYROLYSIS REACTION STUDIES

The laboratory experiments performed in examining the pyrolysis reaction were not novel for the most part, and consisted essentially of using established laboratory procedures for running the pyrolysis reaction. These procedures, developed over the years to achieve a high yield of DQA, consisted of operating with a 5-L round bottom flask fitted with a mechanical paddle agitator (circular segment of Teflon®), an addition flask for adding the DAT feed, and a distillation system. The distillation system consisted of a series of three adapters topped by a Vigreaux column and collection system. A nitrogen purge was maintained on the entire system. Control of the distillation, in reality a progressive partial condensation, was maintained by varying the amount of insulation on the vapor line and column so that the

desired quantity of distillate was taken off at the head of the column. This take-off was a very small fraction of the total boil-up.

Standard boil-up rates were very high (see Table I and Fig. I), and this fact, coupled with the vigorous agitation, normally produced about 2-3 liters of foam in the 5-ℓ. reaction flask, although the normal charge of Dowtherm A (DT) was only 312 grams (about 295 ml). The total feed amounted to only another 355 ml (131 g. of DAT dissolved in 222 g. of DT) and the distillate normally amounted to 167 ml.

Discussions with Dr. W. S. Struve, Dr. P. H. Griswold, Dr. H. H. Gyorgy and Mr. J. M. Wesley indicated some of the major variables affecting yield and quality, and laboratory runs were started to see quantitatively how the operating variables would affect them. The first four runs, Table II, were the initial effort in this direction.

Apart from corroboration of the general trends predicted universally, very little of note occurred in the first two runs. In the third run, Run 8, a noticeable drop in the boiling temperature of the reaction occurred, and was attributed to the presence of alcohol, present in larger than ordinary quantities as a combined result of low boil-up and increased feed rate. In the next run a definite reduction in boiling point was noted, thought it was smaller than in Run 8.

The next observations were made using a 2-ℓ. resin kettle in order to simulate plant operation as to reactor configuration, baffles and agitator design. A definite reduction in yield level was noted, and the agitation pattern, though it gave good mixing, did not appear to provide the action which existed in the 5-ℓ. flask. Foaming occurred, but was more difficult to handle than in the 5-ℓ. flask.

Nitrogen sparging was attempted in an effort to promote alcohol removal. Whether or not the alcohol removal was actually enhanced was not determined. Even at rather low nitrogen rates the reaction mass was cooled appreciably, and plugging of the sparger, whether porous metal or a sparging ring, with DQA caused severe control problems in maintaining nitrogen flow. Failure of the nitrogen flow resulted in an immediate temperature rise and an increase in reaction rate. Since the steady-state concentration of unreacted DAT and MRC is higher at low temperatures, the sudden jump to a high temperature resulted in an increased evolution of alcohol and was equivalent to increasing the feed rate, as was done in Run 8.

The control difficulties alone made nitrogen sparging undesirable, and the decreased reaction rate which is a consequence of the cooling following this mode of operation, was also a step in the wrong direction. Further examination of nitrogen sparging was therefore dropped.

Some of the operation observed in the resin kettle, including that following nitrogen sparging, resulted in poor yields. It was observed generally that poor yields were almost invariably accompanied by a darkening of the alcohol-Dowtherm mixture distilled overhead. When very poor yields were experienced, as in Run 17A, the entire reaction system, including column and condenser, was filled with a persistent fog, which accompanied the development of color in the distillate. The color ranged from light yellow to a murky, brownish orange. This tell-tale indication may be of value in plant operation to spot defective operation. It was quite noticeable in any reaction where bake-out on hot reactor walls occurred. No effort was made to identify the colored substance.

A modest supply of crystallized DAT was available at the start of the program (5094-46). This material was prepared by filtering a solution of DAT in Dowtherm (obtained from the plant) to remove trash and impurities and cooling to crystallize the DAT. The DAT was filtered, washed with methanol to remove Dowtherm, repulped in methanol and again filtered and washed. The crystals were then dried free of methanol. This procedure was followed to prepare additional material, Lot 1845-9. Under standard reaction conditions (Runs 14 and 15) this material was found to give a slightly lower yield of DQA than the 5094-46 material. Whether this difference was due to a different ratio of ethyl-to-methyl groups or to a higher impurity level (there was some difference in the color of the product DQA) was not established. The difference in yield between the two feed materials amounted to an average of less than 1%.

A. Pyrolysis Yield Correlation

If by-product formation leading to yield loss is a result of a reaction between alcohol and DAT or MRC in solution, a secondary reaction is indicated which will have the following rate expression:

$$r_L = k_{L_1} a_{DAT} a_A + k_{L_2} a_{MRC} a_A \qquad (1)$$

where r_L = the rate of by-product formation (moles)(min)$^{-1}$(volume)$^{-1}$

k_{L_1}, k_{L_2} = reaction rate constants for the reaction of alcohol with DAT, MRC respectively, (moles)(min)$^{-1}$(volume)$^{-1}$

a_{DAT} = activity of DAT

a_{MRC} = activity of MRC

a_A = activity of alcohol

Steric factors would indicate that $k_{L_1} = 2k_{L_2}$, and since at steady-state $a_{MRC} = 2a_{DAT}$, equation (1) reduces to

$$r_L = 2K_{L_1} a_{DAT} a_A \tag{2}$$

The general expression for the rate of disappearance of DAT by ring closure in a system to which DAT is being fed constantly is given by

$$r = k_1 a_{DAT} - \frac{F}{Vm} \tag{3}$$

where r = the rate of net disappearance of DAT (moles)(min)$^{-1}$(volume)$^{-1}$

F = DAT feed rate, (moles)(min)$^{-1}$

Vm = reactor volume

k_1 = reaction rate constant for ring closure reaction (moles)(min)$^{-1}$(volume)$^{-1}$

Also, assuming ideal solutions, the steady-state activity of alcohol in the reaction mixture is given by

$$a_A = \frac{R}{KB} = \frac{2F}{KB} \tag{4}$$

where R = the rate of alcohol removal (moles)(min)$^{-1}$

B = the boil-up rate (moles)(min)$^{-1}$

K = the vaporization equilibrium constant

Since two moles of alcohol are formed for each mole of DAT fed, R = 2F.

At steady-state, r = 0 and

$$k_1 a_{DAT} + k_{L_1} a_{DAT} \left(\frac{2F}{KB}\right) - \frac{F}{Vm} = 0 \tag{5}$$

and

$$a_{DAT} = \frac{F}{Vm\left(k_1 + \frac{2k_{L_1} F}{KB}\right)} \tag{6}$$

$$= \frac{KBF}{Vm\,(KBk_1 + 2k_{L_1}F)} \tag{7}$$

At steady-state the yield loss is the rate of formation of by-products divided by the rate of addition of fresh feed:

$$\text{Yield Loss} = L = \frac{r_L}{\frac{F}{Vm}} \tag{8}$$

Substituting equations (2), (4) and (7) into equation (8) gives

$$rL = 2k_{L_1} \cdot \frac{KBF}{Vm(KBk_1 + 2k_{L_1}F)} \cdot \frac{2F}{KB} \cdot \frac{Vm}{F} \qquad (9)$$

which reduces to

$$rL = \frac{4k_{L_1}F}{KBk_1 + 2k_{L_1}F} \qquad (10)$$

Note: k_1 and k_{L_1} are in units of (moles)(min)$^{-1}$(volume)$^{-1}$. The value of k_1 reported by Wesley (KN-66-5) is in units of min.$^{-1}$. and must be multiplied by the molar density of the reaction mass before substitution in the above equations. The above derivations have assumed that the activities are equal to the mole fractions, and for the great dilutions encountered in this reaction the assumption is probably quite accurate.

If one solves equation (10)for the loss rate constant, k_{L_1}, one obtains

$$k_{L_1} = \frac{(L)(KBF)}{4F - 2LF} \qquad (11)$$

Using $k_1 = 0.1283 \frac{\text{lb.-mole}}{\text{min.-ft}^3}$ (converted from Wesley's data) and laboratory data which indicate a fractional yield loss of 0.156 at a boil-up rate of 10 g/min. of Dowtherm and a DAT feed rate of 0.0111 $\frac{\text{g-mole}}{\text{min.}}$ of DAT,

$$k_{L_1} = 2.50 \frac{\text{lb.-moles}}{\text{min.-ft}^3}$$

On substitution of these values back into equation (10) it is seen that the terms in the demoninator become 109 and 0.0555, respectively. Since the $2k_{L_1}F$ term is $<<KBk_1$, it can be neglected in the present range of operating conditions and the yield loss equation simplifies to

$$L = 0.918 \frac{F}{B}$$

The above analysis assumes steady-state operation. The time constants for achieving steady-state after initiation of feed are dependent on the reaction rate constants. Neglecting yield loss reactions, which under normal circumstances will be maintained at low rates,

$$\frac{-da_{DAT}}{dt} = k_1 a_{DAT} - \frac{F}{n_t} \qquad (13)$$

where

F = DAT feed rate (moles)$(min)^{-1}$

n_t = total moles in reaction vessel

Solution of this equation gives

$$a_{DAT} = \left(\frac{F}{k_1 n_t}\right)\left(1 - e^{-k_1 t}\right) \qquad (14)$$

The factor $\left(\frac{F}{k_1 n_t}\right)$ is the steady-state concentration of DAT and the factor $(1 - e^{-k_1 t})$ is the time rate of approach to the steady-state condition. When the term $(1 - e^{-k_1 t})$ is equal to 0.9, t is equal to 5.75 minutes.

A similar analysis of the rate of approach to steady-state for the mono-ring-closed compound would show that something on the order of 13 minutes are required for the attainment of 90% of steady-state concentration. Hence, the assumption of steady-state operation for the purpose of analysis is accurate to the extent of about 85% for laboratory reactions with a duration of 1.5 hours. Accuracy for plant operations should be excellent. Some error might be expected for the thirty-minute laboratory runs.

The yield loss equation (12) strongly indicates the need for maintaining a high boil-up rate. Besides providing improved yield and quality, a high boil-up rate provides a strong damping action for fluctuations in feed rate and boil-up, both of which can have a disastrous effect on yield.

Inherent in the analysis is the assumption of instantaneous mixing. The feed stream enters at a concentration of approximately 0.2 mole fraction and the DAT concentration at steady-state in the reactor is in the order of 0.0014 mole fraction (laboratory). Poor agitation can result in high localized concentrations of DAT, equivalent to a high feed rate. Also, the mass transfer necessary for efficient vaporization is lacking with poor agitation.

Two additional effects are believed to result from good agitation. First, better heat transfer would normally be expected at higher agitation rates, and second, the increased agitation may result in wetting of the heated surfaces, thereby preventing bake-out (reaction on the heat transfer surface in the absence of Dowtherm). It is quite possible that the present plant reaction system may be in frequent trouble because of the latter situation. The reactor is effectively baffled to promote good mixing, and the upper walls of the reactor, bare and hot in the initial part of the reaction, are therefore not well splashed with reaction mix to prevent bake-out. Although the yield results do not show it and the quality results (fluorescence) are somewhat scattered, bake-out appears to be quite undesirable from the standpoint of further processing (lump formation). Since blockage of the upper part of the reactor jacket is not feasible, reduction in the effectiveness of the baffling to permit more swirl up the wall would be the only direct method of wetting the upper reactor wall with existing equipment. Injection of recycled reaction mass in a tangential pattern should also effectively wet the reactor walls and would be a logical extension of putting more heat into the reactor through an external heat exchanger.

Table III and Figure 2 show the correlation of laboratory results with equation 12. In general, the correlation is good. Only three high feed rate runs show any scatter, and some of the difficulty with these may be related to operational difficulties which led to periods of total reflux.

No studies were made showing the effect of charge size on yield. Previous work indicated that there may be such an effect, but equation 12 does not indicate this relationship explicitly. However, implicit in the equation is the assumption of vapor-liquid equilibrium, and increased charge size would adversely affect mass transfer and the ease of attainment of equilibrium. Vaporization efficiency is no problem in the laboratory, where the reaction is run essentially in a foam regime and vapor-liquid equilibrium prevails throughout the reaction mass. Conditions in the plant for achieving vapor-liquid equilibrium are far from ideal and some efficiency factor should be included in the equation to compensate for deviations from tone equilibrium. These deviations would be in the direction of requiring a larger boil-up, because of the lower effective value of K, than is indicated by the equation. Once the efficiency is established, equation 12 should provide a suitable tool for scaling the reactor. As was pointed out above, agitation can affect the efficiency of mass transfer, and equation 12 can possibly be used as a measure of that efficiency.

Since mass transfer efficiency is at least partly dependent on the area available and the diffusional path, it is quite possible that a recirculation system alone, spraying into the reactor free space might greatly improve plant operation. Additional heat input in the recirculation system would be the next logical step. Further increases in vaporization efficiency would be achieved by decreasing the reactor charge relative to the recirculation rate.

Two reaction concepts considered for possible future development involved the use of 1) a higher boiling reaction medium for carrying out the reaction; e.g. TMS, triphenyl, etc., and 2) the use of a spray-dryer-type reactor for developing small droplets in which the reaction could be carried out. The latter scheme, if feasible, presents the possibility of high speed reaction, dry product, and also the possibility of thermally decomposing the DQA to QA, thereby combining pyrolysis and oxidation in a single step.

B. Vapor--Liquid Equilibrium Studies

Several attempts were made to obtain some vapor-liquid equilibrium data. The use of a ternary methanol-ethanol-Dowtherm system was judged to be too difficult to study directly, and consequently the methanol-Dowtherm and ethanol-Dowtherm systems were analyzed separately.

For composition analysis, refractive index was selected, since the method promised speed and good accuracy with small samples. Calibration curves were drawn up, Figures 3 and 4, from data in Table IV. There is evidently in these curves some deviation from ideality.

Some simple calculations, assuming ideal solutions, resulted in the curves shown in Fig. 5 for extremely low concentrations of alcohol such as would be present in the pyrolysis reaction mixture. Initial attempts were made to check vapor-liquid equilibria in this region by doping Dowtherm with alcohol in low concentrations and checking liquid and vapor compositions. The results were not satisfactory.

Two difficulties were immediately apparent. First, the liquid samples had alcohol concentrations too low to determine, and the vapor samples (ca. 2 cc sample from 1 ℓ. of mix) contained water. Careful drying of the ingredients by distillation over lime did not eliminate the water problem. Dr. J. F. Maurer suggested that water adsorbed on the glassware could be causing the difficulty, and suggested oven drying the glassware at 500-600°C. Lack of adequate ovens prevented a follow-up of this suggestion, and a predistillation of the Dowtherm after a period of total reflux was adopted as a substitute measure. Use of larger quantities of alcohol also helped since they prevented any moisture removed from forming a separate phase.

The results of these several determinations are presented in Table V. In general, the liquid samples appear to give reasonable results, and although the methanol-Dowtherm liquid samples appear to have more methanol than was added by synthesis, the synthesis was approximate only and is noted primarily to afford a check of consistency. It is quite evident that these systems deviate considerably from ideal solutions. Vapor-liquid equilibrium data previously used in distillation calculations was that calculated by R. Akell (Engineering Department). These data are presented in Figure 6.

It should be noted that these results are "horseback" evaluations of the vapor-liquid equilibria, and are barely representative of steady-state, let alone true equilibrium. However, they can provide a first approximation to the alcohol-Dowtherm system, and offer a guide to calculations in the system. No attempt has been made to calculate activity coefficients for these systems.

If further work in this area is undertaken, something closer to an equilibrium still should be employed, and an improved sampling procedure should be used.

In plant operation the initial distillation of Dowtherm is observed at about 270°C. There has been concern about this discrepancy with the "normal" boiling point of 257.7°C., and several attempts have been made to resolve the discrepancy. Since this amount of boiling point rise is the result of only 4.0 psig pressure on the system, which normally operates at a pressure of 2.08 psig, and occasionally as much as 3.6 psig, the added effects of liquid head in the pyrolysis tank and pressure drop from the tank to the pressure tap can easily account for the remaining 0.4 to 2.0 psig.

C. Plant Heat Input Determination

A chart was selected from plant records showing the time-temperature trace of a Dowtherm charge in the pyrolysis tank. The temperature data were transformed into enthalpy values and are shown in Figure 7. The slope of this curve is the heat input rate. Based on an assumed charge of 1045 gallons of Dowtherm and an inlet temperature of 318°C for the heating Dowtherm and Dowtherm flow rate of 100 gpm, the following table can be calculated:

Time, min.	Temp., °C.	H_2 Btu/lb.	ρ lbs./ft^3	$q = \frac{dQ}{dQ}$ 10^6 Btu/hr.	Heat Trans. Area, ft^2	DT outlet Temp. °C.	ΔT °F	Overall Heat Trans. Coeff.* Btu/hr ft^2 °F
0	150	103.3	59.64	0.976	107.5	293.8	280	32.4
15	186	133.9	57.61	0.955	110.6	294.4	216	40.0
30	217.5	161.8	55.74	0.947	113.7	294.6	160	52.1
45	249	190.4	53.83	0.907	117.1	295.5	104	74.5
60	264.9	205.0	52.84	0.277	119.0	314.6	89.5	26.0
75	269.4	209.8						
90	270	210.3						

* $U = \frac{q}{A\ \Delta T}$

Calculations of the heat transfer area were based on figures of J. W. Wesley who reported the following:

Head area	41.5 ft^2 (1.5 ft^2 at drain removed)
Head volume	34 ft^3
Cylindrical area	20 $ft^2/ft.$
Cylindrical volume	32 $ft^3/ft.$

The reason for the variation in heat transfer coefficient with temperature is difficult to explain. The basic reason for this variation is the relatively uniform heat input rate observed over much of the heat-up cycle, despite the decreasing ΔT, and may result from a distortion of the time-temperature record by the recorder.

PGReis/mja
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TABLE I

LABORATORY HEAT INPUTS AND BOIL-UP RATES

Mantle	Variac Setting	Mantle Current Amps	Heat Input Watts	Boil-up Rate g DT/min.
5-1 Flask	95	3.8	318	9.64
	108	4.4	426	24.65
	120	4.9	528	42.15
	140	5.5	666	66.87
Resin Kettle	95	3.6	304	11.4
	100	3.8	338	19.2
	120	4.6	495	39.7
	140	5.3	658	49.5

5-1. Flask Mantle	22.0 Ω
2-1. Resin Kettle Mantle	23.4 Ω

TABLE II

PYROLYSIS REACTION SUMMARY

Std. Charge: 312g DT in Flask; Feed-131g DAT in 222g DT

Run No.	Reaction System	Variac Setting	Pot Temp. °C DT	Pot Temp. °C Reaction	Feed Time, min.	DQA Yield g.	Fluor-escence	DAT Feed	Comments
6	5-1. Fl.	140	258	257	90	99.7	101	5094-46	
7	"	96	256	255+	90	93.7	52	"	
8	"	96	258	254	30	84.6	27	"	
10	"	110	258	256.7	90	98.8	98.6	"	
11	2-1. Res. K.	100	255	255	90	95.4	84.0	1845-9	
12	"	120	255	254	90	96.2	87.0	"	Bake out. DPU.
13	5-1. Fl	140	257	256+	30	93.8	75.0	"	
14	"	140	257	256+	90	98.7	92.6	"	
15	"	140	258	256+	90	98.9	98.1	"	
16	"	100	256+	256	90	96.8	93.0	"	
17	2-1. Res. K.	120	256+	256	90	96.8	93.0	"	Bake-out. No baffles
17A	"	95	239	214	90	63.2	48.8	"	Nitrogen sparging
18	"	110	244	248	90	84.5	40.5	"	Nitrogen sparging
19	"	110	247	248	90	91.5	54.0	"	Nitrogen sparging
20	5-1. Fl.	120	257	255	30	90.5	68.3	"	Poor control-total reflux
21	"	120	255.4	254.2	90	97.7	82.5	5094-46	
22	"	140	255.5	255.35	90	98.9	90.9	"	
23	"	96	255.5	253.1	90	94.1	87.0	"	
24	"	96	255.9	252.8	30	83.0	57.0	"	
25	"	140	255.7	255.5	30	93.9	65.4	"	

TABLE III

PYROLYSIS YIELD LOSS CORRELATION

Run	Yield g. DQA	Corrected[1] Yield, %	Yield Loss, %	F/B
6	99.7	99.2	0.8	0.00918
7	93.7	93.2	6.8	0.0569
8	84.6	84.2	15.8	0.1706
10	98.8	98.3	1.7	0.0215
13	93.8	93.3	6.7	0.0276
14	98.7	98.2	1.8	0.00918
15	98.9	98.4	1.6	0.00918
16	96.8	96.3	3.7	0.0386
20	90.5	90.0	10.0	0.0444
21	97.7	97.2	2.8	0.0148
22	98.9	98.4	1.6	0.00918
23	94.1	93.6	6.4	0.0569
24	83.0	82.5	17.5	0.1706
25	93.9	93.4	6.6	0.0276

1. Correction is based on yield loss approximation,
$L = 0.918 \frac{F}{B}$ calculated from a single point.
This correction affects only the overall yield level.

TABLE IV

REFRACTIVE INDEX VS. COMPOSITION FOR SYSTEMS METHANOL-DOWTHERM AND ETHANOL-DOWTHERM

System	N_d^{20}	Mol Fraction Alcohol	Grams Alcohol	Grams Dowtherm
Meth.-DT	1.3301	1.0000	-	-
	1.3720	0.9625	1.5979	0.4011
	1.4176	0.8861	1.2005	0.7996
	1.4700	0.7752	0.7984	1.1991
	1.5348	0.5629	0.3980	1.6006
	1.5905	0.0000	-	-
Eth.-DT	1.3624	1.0000	-	-
	1.3991	0.9350	1.5979	0.3990
	1.4412	0.8437	1.1986	0.8000
	1.4849	0.7056	0.7982	1.1995
	1.5348	0.4759	0.4036	1.6009
	1.5905	0.0000	-	-

TABLE V

LIQUID-VAPOR BOILING COMPOSITIONS
FOR METHANOL-DOWTHERM AND
ETHANOL-DOWTHERM

System	Type Sample	Temperature °C.	Mol Fraction Alcohol Synthesis	Analysis[1]	Calculated[2]
Eth.-DT	Liquid	206.0	0.035	0.000	0.0226
	Vapor	166.3		0.931	0.924
	Liquid	139.3	0.100	0.063	0.1333
	Vapor	105.3		0.972	0.996
	Liquid	112.5	0.159	0.107	0.301
	Vapor	91.5		0.978	0.999
	Liquid	93.0	0.286	0.258	0.581
	Vapor	79.0		0.986	0.999
Meth.-DT	Liquid	164.0	0.035	0.015	0.030
	Vapor	118.3		0.979	0.989
	Liquid	96.0	0.100	0.099	0.340
	Vapor	74.4		0.994	0.999
	Liquid	80.0	0.159	0.200	0.576
	Vapor	68.0		0.995	0.999

1. Analysis based on refractive index measurement.
2. Calculated on the basis of ideal solution.

K+E 20 X 20 TO THE INCH KEUFFEL & ESSER CO. 359-10½G MADE IN U.S.A.

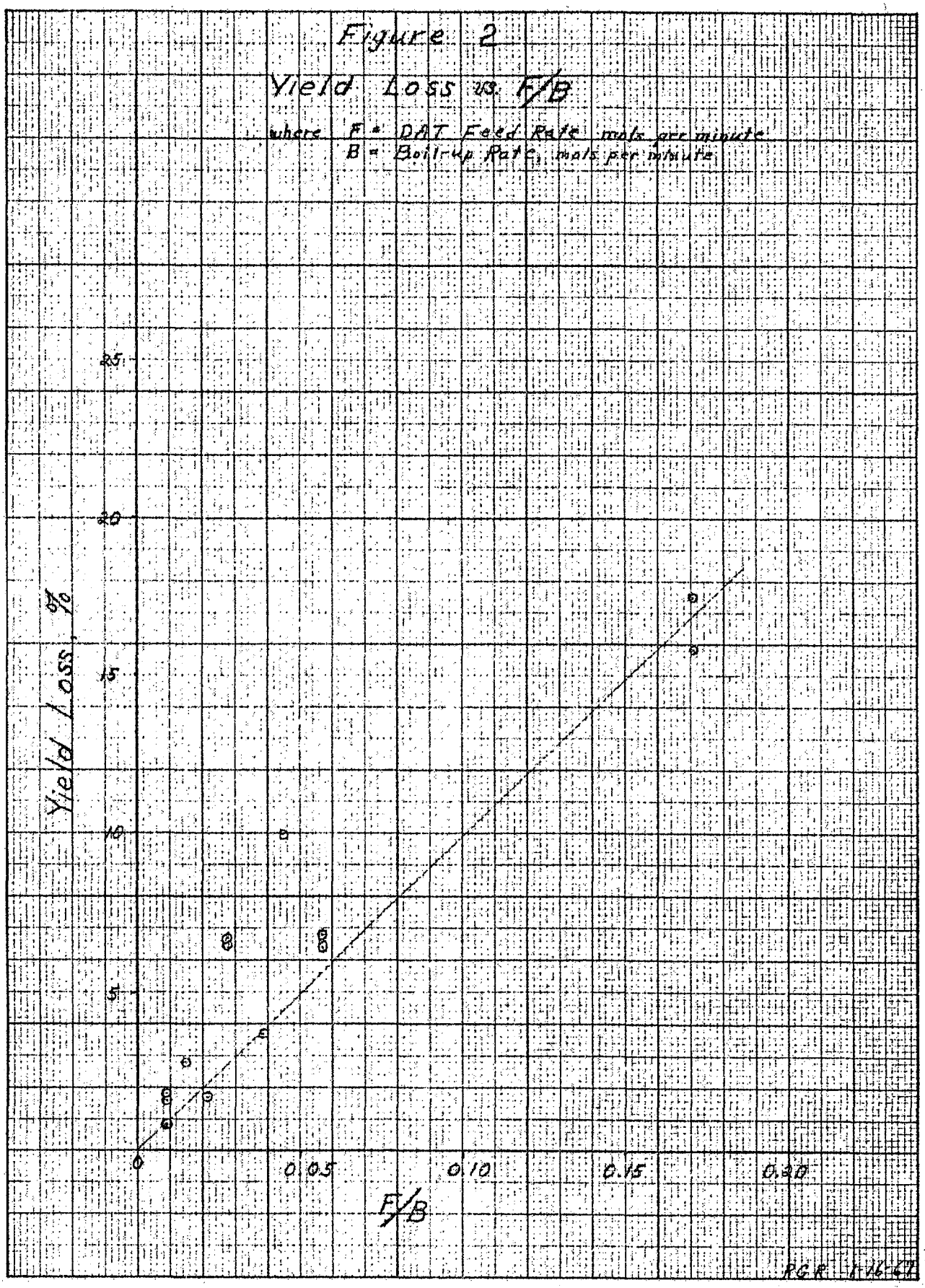
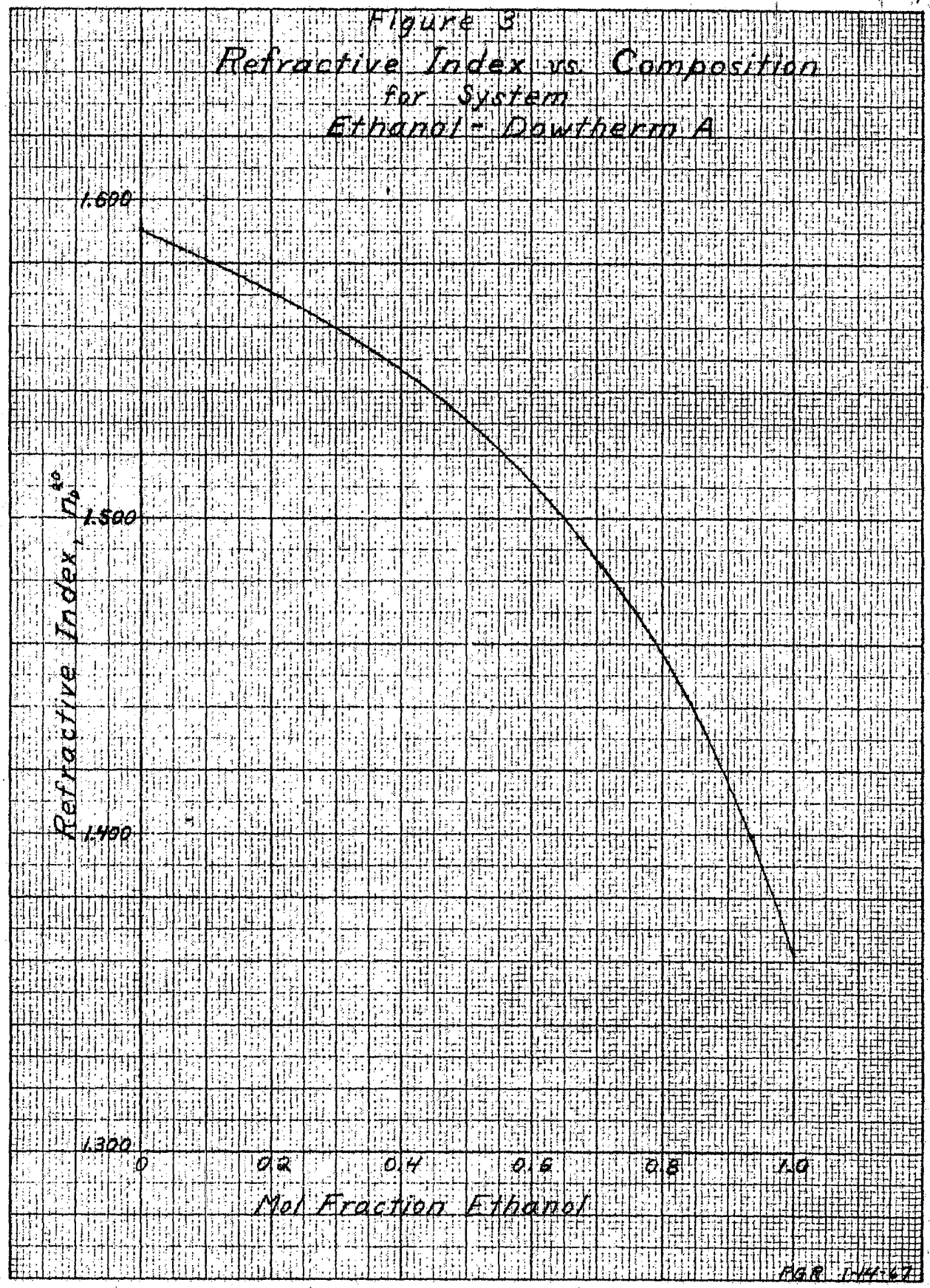


Figure 3

Refractive Index vs. Composition
for System
Ethanol - Dowtherm A



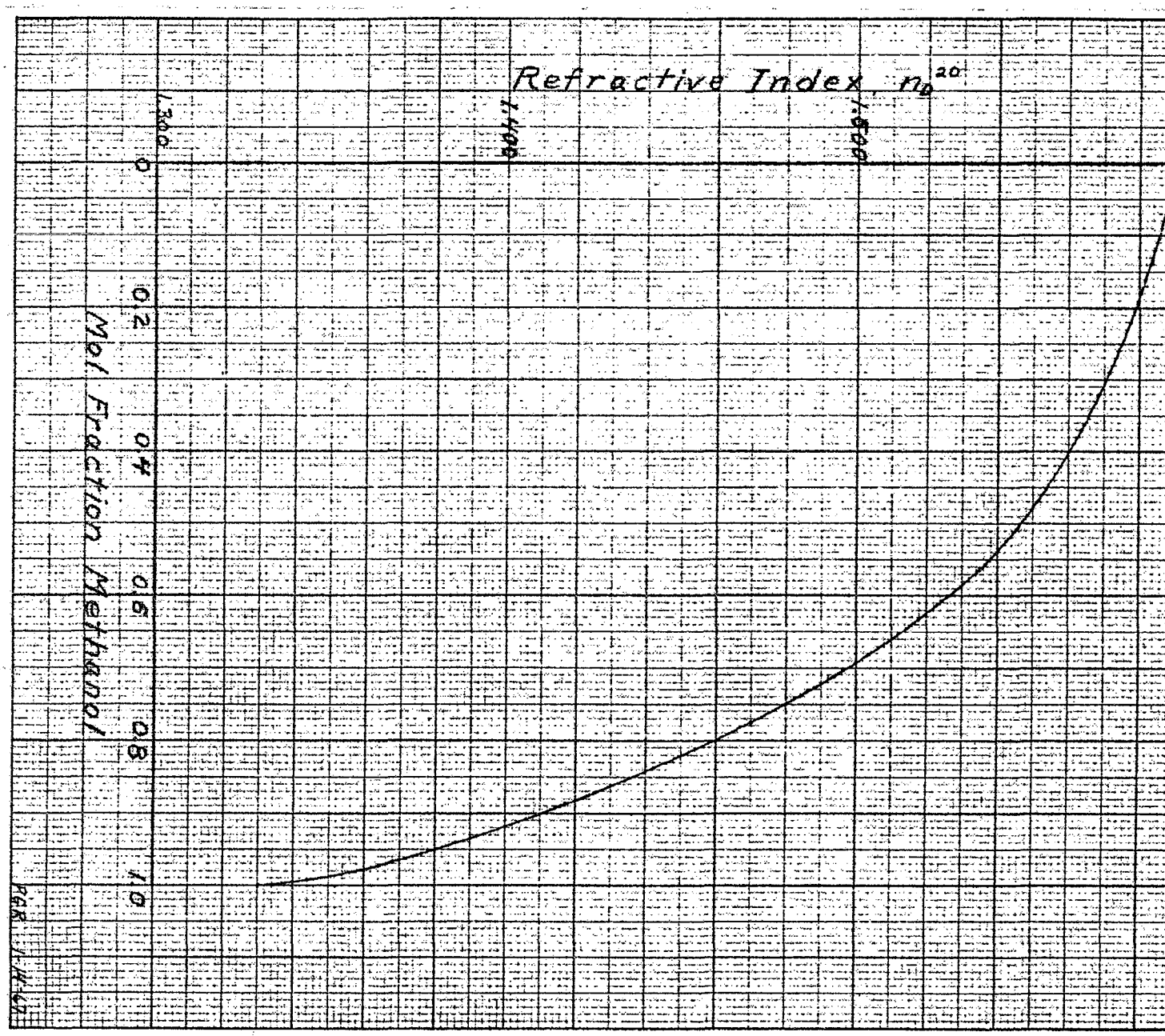
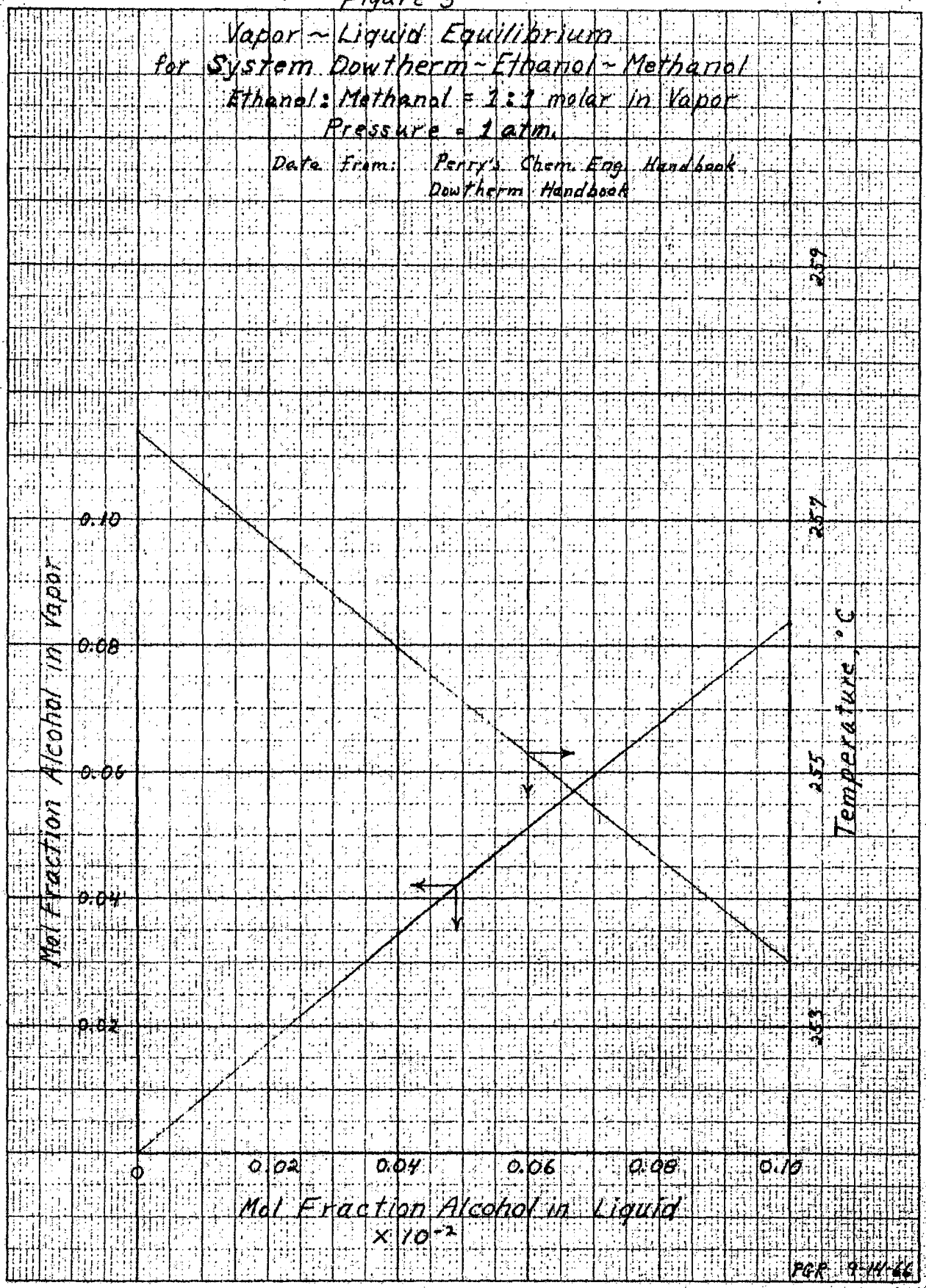


Figure 5

Vapor ~ Liquid Equilibrium
for System Dowtherm ~ Ethanol ~ Methanol
Ethanol : Methanol = 1 : 1 molar in Vapor
Pressure = 1 atm.

Data From: Perry's Chem. Eng. Handbook
Dowtherm Handbook



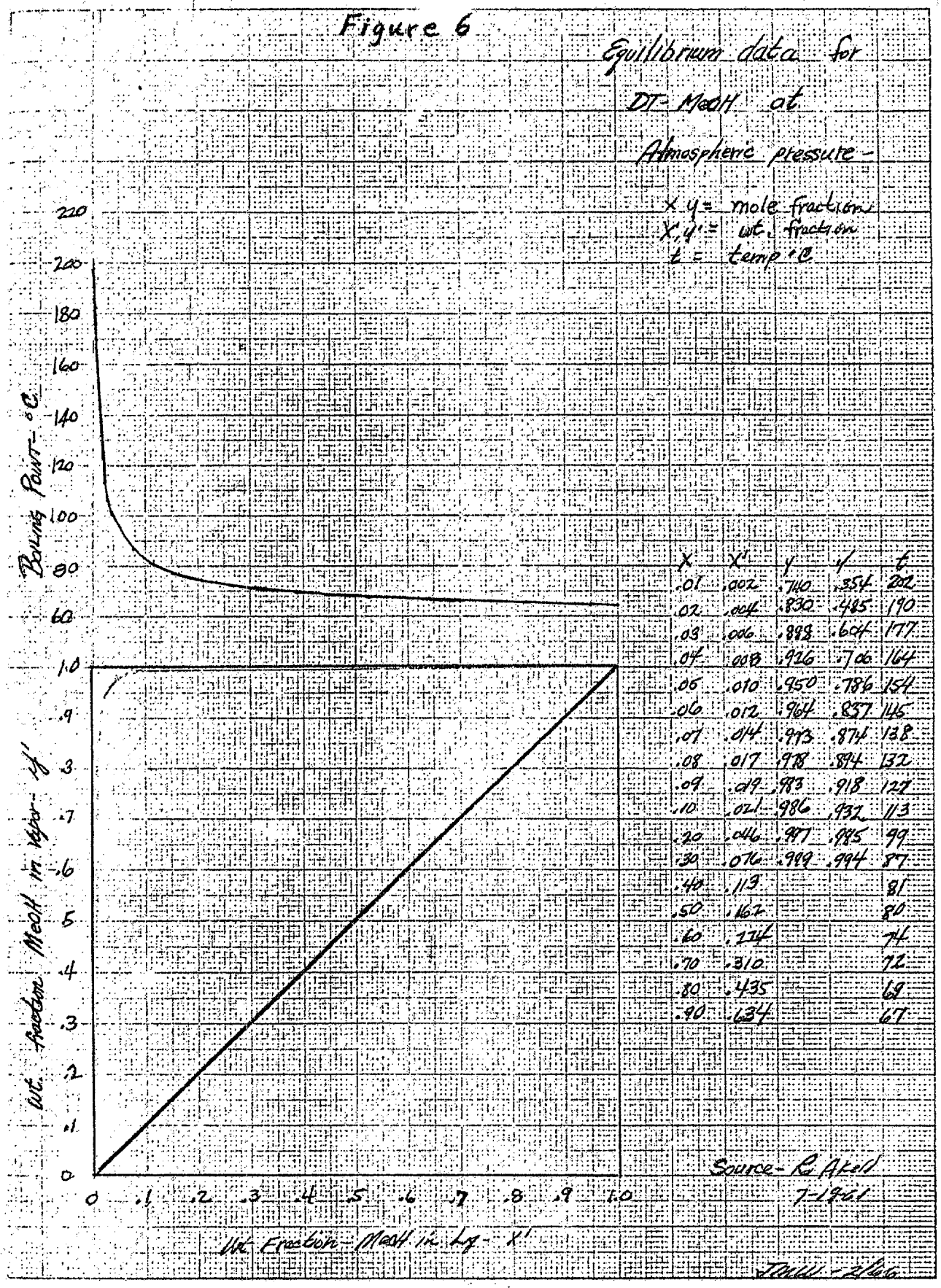
EUGENE DIETZGEN CO.
MADE IN U.S.A.

NO. 341-20 DIETZGEN GRAPH PAPER
20 X 20 PER INCH

Figure 6

Equilibrium data for DT-MeOH at Atmospheric pressure -

x, y = mole fraction
x', y' = wt. fraction
t = temp °C



x	x'	y	y'	t
.01	.002	.740	.354	202
.02	.004	.830	.485	190
.03	.006	.882	.604	177
.04	.008	.926	.706	164
.06	.010	.950	.786	154
.06	.012	.964	.837	146
.07	.014	.973	.874	138
.08	.017	.978	.894	132
.09	.019	.983	.918	127
.10	.021	.986	.932	113
.20	.046	.997	.985	99
.30	.076	.999	.994	87
.40	.113			81
.50	.162			80
.60	.214			74
.70	.310			72
.80	.435			69
.90	.634			67

Source - R Akell 7-1961

Tau - Plot

Figure 7

Heat Input to Dowtherm Heel Pyrolysis Tank

Heating Dowtherm at 300°C (273 - 303° Range)