

KN-70-5 SUBSTITUTED QUINACRIDONES By: L. R. Lerner 6/68 - 4/69

1/79 (1)

~~(13) R. Klar~~

~~10/9/80~~

~~(13) J. L. Bauman~~

~~8/31/81~~

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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

SUBSTITUTED QUINACRIDONES

Period Covered June, 1968 to April, 1969

FILE: 223.91

DATE: 1/30/70

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NEWARK PLANT

PIGMENT COLORS RESEARCH REPORT

SUBJECT: SUBSTITUTED QUINACRIDONES

PERIOD COVERED: June, 1968 to April, 1969

SUBMITTED BY: L. R. LERNER

DATE SUBMITTED: 12/15/69

APPROVED BY: F. F. EHRICH

DATE RELEASED: 1/30/70

ABSTRACT

A series of new substituted quinacridones (2,3,9,10-tetrachloro-, 2,9-diacetyl-, 2,9-diacetamido-, and 2,9-dimethylsulfonyl-QA) were prepared for evaluation as pigmentary materials, and for the determination of the effect of these 2,9-substituents on viscosity behavior in paint systems. All of these substituted quinacridones showed poor lightfastness both in acrylic enamel and acrylic lacquer. They all showed relatively low viscosity in both systems, but a blend of RT-849-D and 2,9-diacetylQA showed a decrease of viscosity that would be expected by a simple additive effect.

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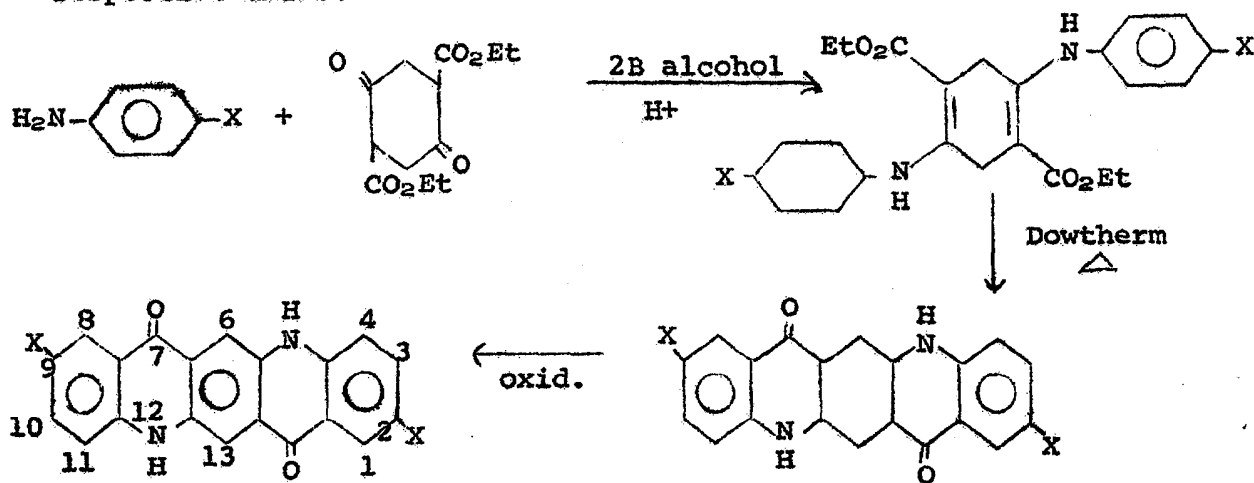
I. INTRODUCTION

Certain quinacridones (QA's) being used in automotive finishes show rather high viscosities in certain paint vehicles. High viscosity presents a problem in spraying and in reflow, so that it would be desirable to modify the quinacridone in order to improve its rheological properties with respect to this application. A select series of 2,9-substituted QA's were prepared, therefor, which had large differences in Hammett σ_p function: acetyl (+0.516), acetamido (-0.015), methylsulfonyl (+0.728). In addition, the 2,3,9,10-tetrachloroQA was also prepared and evaluated.

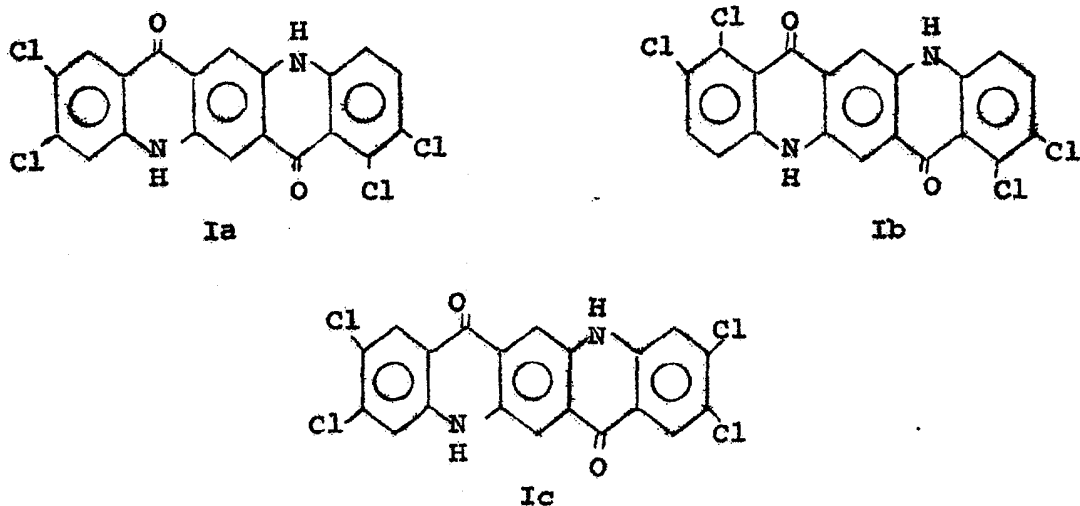
II. RESULTS AND DISCUSSION

Preparation

The substituted QA's were prepared as follows from the respective amine.



In the case of 2,3,9,10-tetrachloroQA (Ic), there are three possible products (Ia,b, and c) when starting with 3,4-dichloroaniline.



It has been shown by others that substitution in the 1 or 4 (8 or 11) positions cause greater solubility than substitution in the 2 or 3 (9 or 10) position. Assuming this greater solubility, the crude tetra-substituted QA was repeatedly acid crystallized and the least soluble product used in this study. (The acid crystallization was repeated until there was no change in the infrared spectrum - see below.)

Solubility

It seemed desirable to determine what effect these substituents would have on solubility. This is of particular interest in plastics applications (e.g., quinacridone is partially soluble in nylon, therefore restricting its application in this plastic). Using a procedure developed by H. Matrick (see Experimental), it was determined that all the new disubstituted QA's had a solubility of < 0.014 g/l in boiling 1-chloronaphthalene (unsubstituted QA has a solubility of 0.084 g/l).

In an attempt to find a more sensitive solubility measure, the refluxing 1-chloronaphthalene slurries were checked for fluorescence with a long wavelength ultraviolet lamp. (Ultraviolet Products, Inc. UVL-21 lamp.) The results show that the 2,9-di-acetamido and the 2,9-dimethylsulfonyl QA do not fluoresce, while 2,9-diacetyl does show some green emission. These results would indicate a slightly higher solubility for the latter. This assumption was confirmed by the faster crystallite growth rate of 2,9-diacetyl QA in refluxing DMF (electron micrograph). As was anticipated from the low solubilities found, none of the samples showed any color change when extruded in polystyrene at 400 and 600°F. respectively. Due to poor lightfastness, this was not pursued further.

Viscosity

It was expected that by placing electron-donating or withdrawing groups on quinacridone, the viscosity might be decreased. Table I shows that these substituted QA's do show decreased viscosity, but a blend of RT-849-D and 2,9-diacetyl QA does not show as marked a decrease as would be desired.

Table I

Brookfield Viscosity Measurement
Acrylic "Lucite" 11/4/69

<u>Quinacridone</u>	<u>Spindle #</u>	<u>6</u>	<u>RPM</u>	<u>12</u>	<u>30</u>	<u>60</u>
2,3,9,10-tetraCl	2	6.5		11.5	24.5	47.5
diacetamido (large particle)	2	3.0		5.5+	13.5+	27.0
" (HF-milled)	2	3.0		6.0	14.5+	29.0
diacetyl (large particle)	2	4.5		8.0	17.0+	32.5+
" (HF-milled)	2	19.0+		33.0+	63.0	99.5+
dimethylsulfonyl (α phase, large particle)	2	3.0		5.0	12.0+	24.0+
RT-792-D, 86979	2	59.0		+73.0	Off scale	
	3	16.5		20.5+	29.5	40.5
RT-849-D, 90158	2	26.0+		35.0+	50.5	83.5
RT-742-D, 00117	2	19.0		29.5	41.0	67.0

<u>Quinacridone</u>	<u>6</u>	<u>12</u>	<u>RPM</u>	<u>30</u>	<u>60</u>
2,9-diacetyl (large particle)	1.0	1.5		3.0	6.0
" (HF-milled)	0.5	1.0		2.5	5.5
Tetrachloro (HF-milled)	1.5	2.3		5.0	9.0
2,9-diacetamido (large particle)	0.5	1.2		2.8	5.5
" (HF-milled)	0.7	1.2		2.8	6.0
2,9-dimethylsulfonyl (HF-milled - β -phase)	1.5	2.8		6.2	12.0
RT-792-D, SL-86979	7.0	10.0		16.0	23.0
RT-849-D, PS-90158	50.0	56.5		68.0	82.5
RT-742-D, PS-00117	7.0	9.5		13.0	20.5
RT-795-D, 97189	4.5	6.5		10.5	16.0

<u>Quinacridone</u>	<u>6</u>	<u>4/3/69</u> <u>12</u>	<u>#3 Spindle</u> <u>30</u>	<u>60</u>	<u>Ford</u> <u>Cup</u>
2,9-diacetyl (disp.milled) (1897/61A)	1.0	1.5	3.5	6.2	27"
RT-792-D	1.7	3.2	7.0	12.5	41"
RT-849-D	2.7	30.5	37.5	46.2	100"
		<u>4/18/69</u>	<u>#3 Spindle</u>		
1897/61A 10%, RT-849-D 90%	1.7	20.0	25.3	32.3	
RT-849-D, PS-90158	24.0	28.0	35.2	44.0	

Color and Lightfastness

For each of the 2,9-disubstituted QA's, two phases were found (though there may be more). The least stable (α) phase of each, except 2,9-dimethylsulfonyl, was obtained by acid crystallization and the more stable (β) from DMF refluxing or dispersion milling. The α -phase of the methylsulfonyl derivative was obtained directly from its synthesis, but both acid crystallization and DMF reflux gave β -phase. Table II shows the X-ray data for each compound (also see appendix).

Table II

X-Ray Diffraction Data
 α -phase from acid crystallization*
 β -phase from DMF reflux
w = weak
m = medium
s = strong

<u>Quinacridone</u>	<u>Phase</u>	<u>X-Ray Peaks</u>
2,9-diacetamido	α	7.6(w), 9.0(w), 14.1(s), 17.0(s), 25.2(vs) 25.9(s), 28.4(m)
"	β	4.8(s), 17.4(w), 19.0(w), 20.6(w), 25.9(vs) 28.2(m).
2,9-diacetyl	α	4.4(s), 8.8(w), 14.0(w), 27.0(vs).
"	β	4.8(s), 9.8(w), 13.8(m), 15.9(w), 18.9(w) 19.7(w), 25.6(w), 26.7(vs), 28.6(w).
2,9-dimethylsulfonyl	β	7.0(w), 13.6(m), 16.8(vs), 19.0(w), 20.6(m), 22.0(m), 23.4(s), 24.7(w), 26.4(w), 27.2(m), 28.0(m), 28.9(vs).
	α	5.0(w), 9.9(w), 13.0(m), 14.9(w), 17.4(w), 18.9(w), 19.9(s), 20.9(w), 24.2(m), 25.4(vs), 28.0(m).

*except 2,9-dimethylsulfonyl; crude product from synthesis is α , β from both DMF reflux and acid crystallization.

The color differences between each of the phases is quite marked, particularly in the case of the 2,9-diacetylQA (see appendix for reflection spectra). Table III shows longest wavelength absorptions of each QA.

Table III

Longest Wavelength Absorption of Some Quinacridones

<u>Compound</u>	<u>Phase</u>	<u>Vehicle</u>	<u>max (nm)</u>
2,9-diacetylQA	α	Zinc oxide drawdown	602
"	β	TAE-3 or acrylic "Lucite"	558
2,9-diacetamidoQA	α	Zinc oxide drawdown	576
"	β	" "	614
"	β	TAE-3 or acrylic "Lucite"	614
2,9-dimethylsulfonylQA	α	Acrylic "Lucite"	546
"	β	" "	550
"	β	TAE-3	550
2,3,9,10-tetrachloro	-	Acrylic "Lucite" or TAE-3	556

All β -phase (and α of 2,9-dimethylsulfonylQA) were exposed in Florida. The results in TAE-3 and acrylic "Lucite" are shown in Table IV. In each case, there is a marked "break" in all the panels after three months, thus indicating poor lightfastness.

TABLE IV

OUTDOOR DURABILITY

S-68468

<u>Panel</u>	<u>Pigment</u>	<u>Initial Gloss 20°</u>	<u>6 Mos.</u>
<u>Metallics 10/90 Al/Toner P/B 15/100</u>			
1	1897-13B-1	46	7f
2	38	45	6f
3	38-1	49	6f
4	39	69	6f
5	39-1	49	6f
6	40C	71	3f
7	RT-792-D, SW-86979	45	7f
8	RT-849-D, 90158	46	9f
9	RT-742-D, 00117	45	9.5f
<u>Tints 5/95 Toner/White</u>			
10	1897-13B-1	63	3f
11	38	68	4f
12	38-1	73	4f
13	39	63	3f
14	39-1	62	3f
15	40C	70	0
16	RT-792-D	78	4f
17	RT-849-D	74	5f
18	RT-742-D	76	4f

- 6 -
S-69431

<u>Panel</u>	<u>Pigment</u>	<u>Al/Toner</u>	<u>Initial Gloss 20°</u>	<u>3 Mos.</u>
1	1897-61A	10/90	63	7f
2	RT-792-D, 86979	"	68	10
3	RT-849-D, 90158	"	60	10
5/95 Toner/White				
4	1897-61A		61	5f
5	RT-792-D, 86979		60	10
6	RT-849-D, 90158		61	10

S-69406

<u>Panel</u>	<u>Pigment</u>	<u>Al/Toner</u>	<u>P/B</u>	<u>Init. Gloss 20°</u>	<u>3 Mos.</u>
1	1897-55B	10/90	0.15	72	7f
2	54C	"		73	5f
3	45B-2	"		64	6f
4	45C	"		62	6f
5	52G	"		71	3f
6	RT-792-D	"		77	9.5f
7	RT-849-D	"		49	10
8	RT-742-D	"		71	10
9	RT-795-D	"		64	10
10	1897-55B	50/50	0.97	65	8f
11	54C	"		66	6f
12	45B-2	"		63	8f
13	45C	"		60	7f
14	52G	"		63	3f
15	RT-792-D	"		64	9.5f
16	RT-849-D	"		60	10-
17	RT-742-D	"		67	10
18	RT-795-D	"		63	10
Tints 5/95 Toner/White					
19	1897-55B			70	9.5
20	54C			72	6f
21	45B-2			69	8f
22	45C			66	6f
23	52G			70	3f
24	RT-792-D			72	10
25	RT-849-D			71	10
26	RT-742-D			73	9f
27	RT-795-D			69	9f

The poor lightfastness of these compounds relative to quinacridone could be due to poor packing in the crystal due to the substitution. This could cause a decrease in the ability of the excited molecule to dissipate its energy by non-reactive pathways. It is also quite possible that the substituents themselves (e.g., acetyl or acetamido) are photoreactive. Whatever the reason, these substituents are detrimental to lightfastness.

EXPERIMENTAL

All infrared spectra were recorded on a Perkin-Elmer Model 21 or Model 137. The preparation of 2,9-diacetylQA was typical.

Diethyl-2,5-di(4'-acetylanilino)-3,6-dihydroterephthalate

To a 3 liter flask equipped with agitator, thermometer and N₂ inlet, was added

51.2 g (0.2 mole) of diethyl succinylsuccinate and 1 liter of 2B alcohol. The flask, under nitrogen, was heated until solution occurred. Then 91 g (0.6 mole) of p-aminoacetophenone and 6 ml (0.070 mole) of concentrated HCl were added. The solution was refluxed for 3 hrs., cooled to 50°C. and filtered. The product was reslurried in 2B alcohol and stirred with a solution of 7.2 g Na₂CO₃ in 25 ml H₂O for 10 minutes. The product was filtered, washed Cl⁻ free and dried.

Yield: 88 g (90%, mp 222-224°).

Using p-aminoacetanilide, 90 g (0.6 mole) instead of p-aminoacetophenone and CF₃CO₂H, 5.2 ml (0.070 mole) instead of HCl, a yield of 103.7 g (theoretical 104 g) was obtained (mp 294-296°C).

Using 3,4-dichloroaniline (97.2 g, 0.6 mole) as the amine and CF₃CO₂H, the yield of the corresponding dichloroanilinoterephthalate was 107 g (theoretical 109 g, mp 208-210°C.).

In order to obtain good yields using p-aminophenylmethylsulfone, n-butanol and CF₃CO₂H were used instead of 2B alcohol and HCl. This reaction was run 10 hrs. on half scale using 50 g (0.30 mole) of p-aminophenylmethylsulfone. Yield 52.0 g (92%, mp 167-180°).

2,9-Diacetyldihydroquinacridone

In a 5 liter flask equipped with an agitator and Dean-Stark tube, 2 liters of distilled "Dowtherm" was heated to reflux. Under a nitrogen atmosphere, 88 g of diethyl-2,5-di(4'-acetylaniline) 3,6-dihydroterephthalate was added portionwise. The ethanol generated was allowed to come off during and after addition. After all the ethanol was removed, the solution was refluxed for an additional 2 hrs. The solution was cooled to 50-60°, filtered and washed with methanol. The product was slurried in methanol, filtered, and dried. The yield was 69 g (96%, mp > 360°).

The corresponding diacetamidodihydroquinacridone was obtained in quantitative yield (mp 360°) by this procedure. The yields of dimethylsulfonyl and tetrachlorodihydroquinacridone was 91% and 88% respectively (both mp > 360°C.).

2,9-Diacetylquinacridone

In a 2 liter flask equipped with an agitator and condenser was placed 280 ml water, 75 g sodium hydroxide and 48 g (0.12 mole) 2,9-diacetyldihydroquinacridone and 375 ml of methanol. After the solution was stirred for 1.5 hrs., a solution of 28.2 g (0.13 mole) of sitol in 115 ml of water was added. After refluxing for 2 hrs., the slurry was flooded to 10 liters with water, filtered, washed alkali-free (brilliant yellow paper) and dried. The yield was 45.3 g (95%, mp 360°C.).

The yields of 2,9-diacetamido-, 2,9-dimethylsulfonyl-, and 2,3,9,10-tetrachloroquinacridone were 87, 75, and 88% respectively.

These samples were purified by sulfuric acid crystallizations and hot DMF extractions. In the case of the tetrachloroquinacridone, four acid crystallizations were carried out in order to obtain a product which did not change by ir.

Solubility Determinations

Pigment solubilities were determined by heating a known weight of pigment (typically 10 to 100 mg) in a flat bottom flask (500 ml) with various amounts (100 ml and up) of solvent (typically 1-chloronaphthalene). The flask was equipped with a reflux condenser and thermometer placed through the condenser. Stirring was done magnetically and the extent of solution observed by shining an intense beam of light through the flask. See the discussion sections for the results.

dc

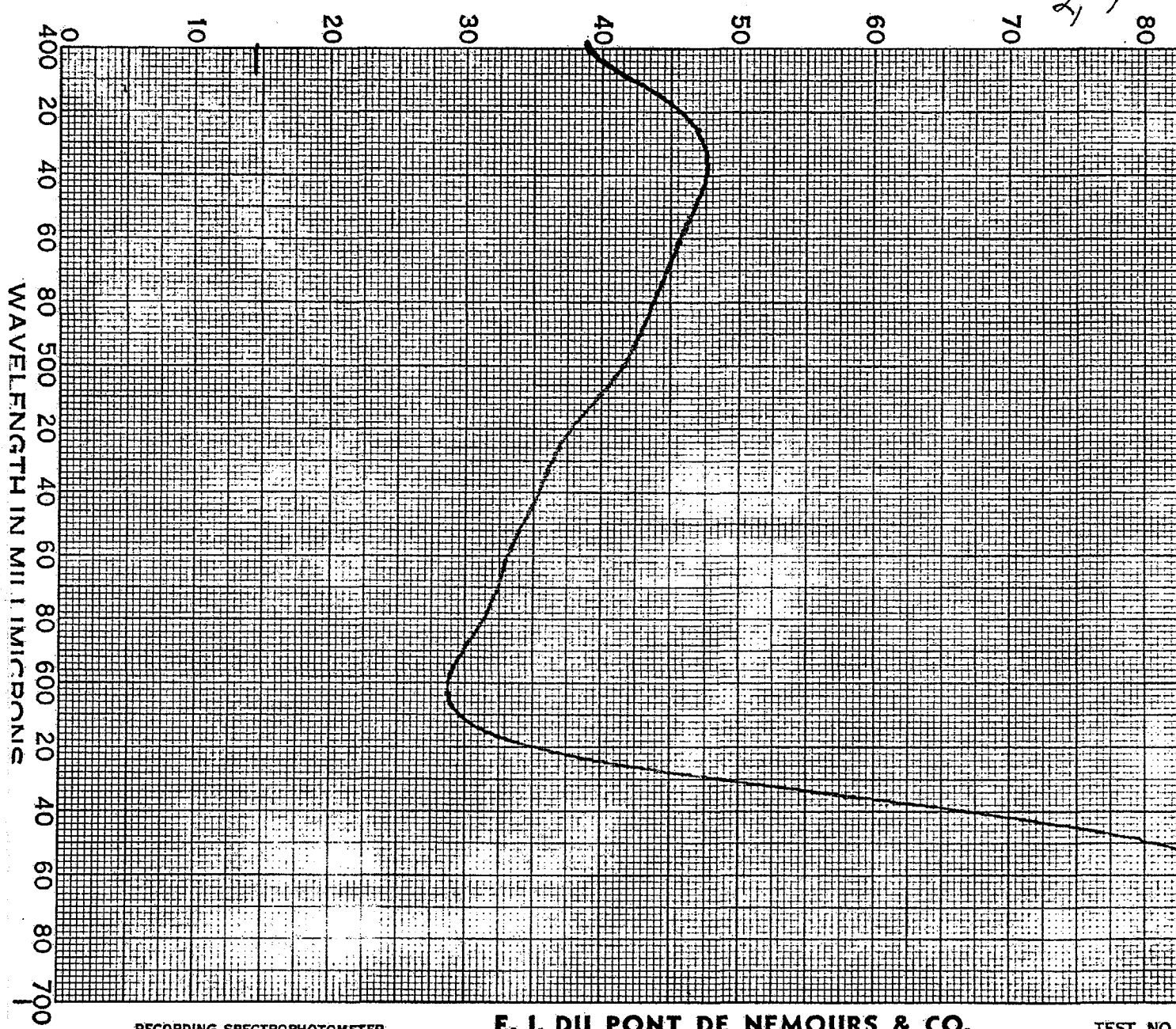
APPENDIX I

REFLECTANCE SPECTRA

1897-
2,9-180

in 0 draw down

REFLECTANCE
TRANSMITTANCE (PERCENT)



RECORDING SPECTROPHOTOMETER

INSTRUMENT NO. 2646334

E. I. DU PONT DE NEMOURS & CO.

PIGMENTS DEPARTMENT

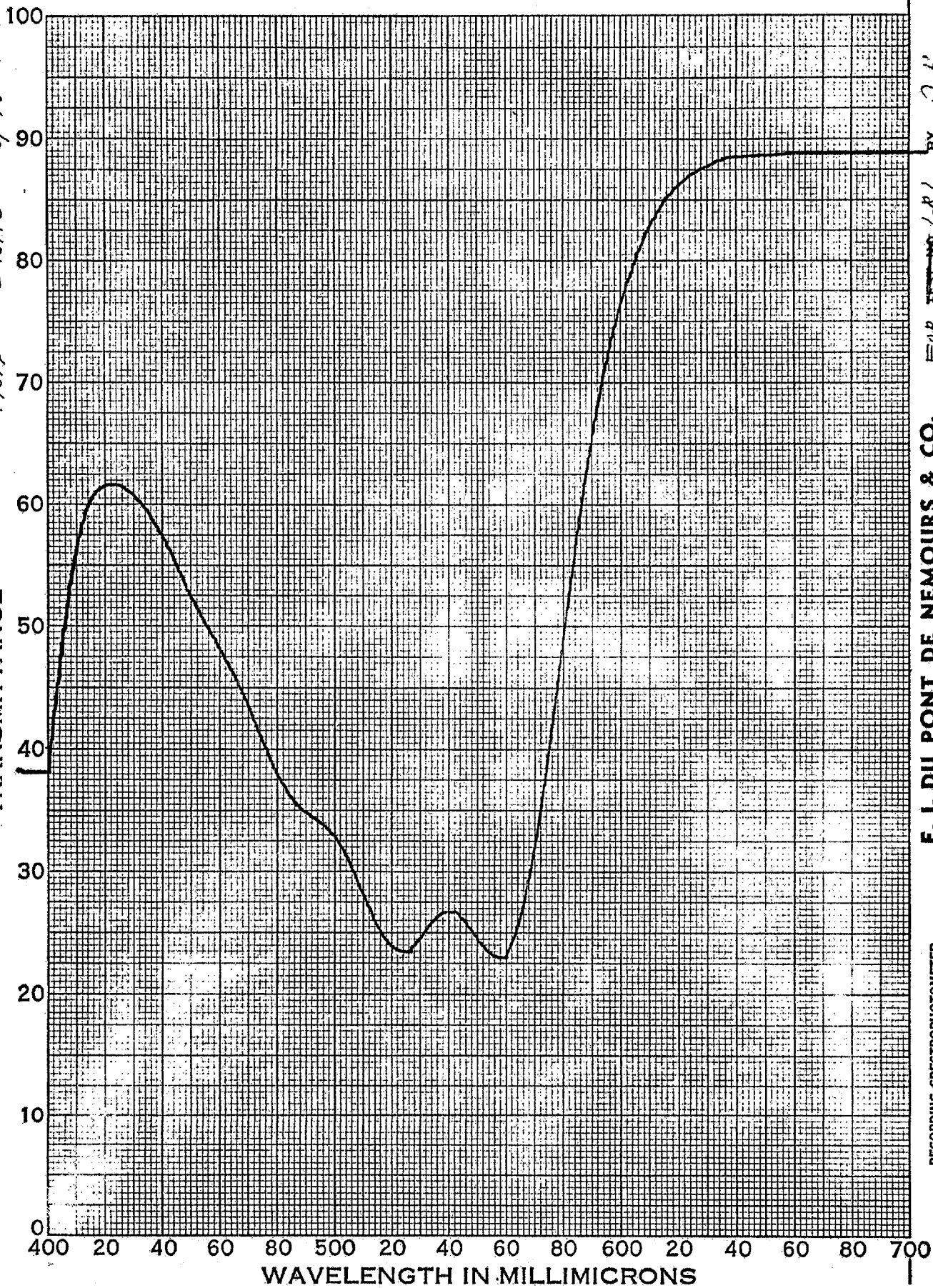
TEST NO.

DATE

DUP050081953

3,9-Diacetyl QA (4F mlU) 68-744 A 1297-39-1
Acrylic Lacite 5/95 Tint

REFLECTANCE
TRANSMITTANCE (PERCENT)



RECORDING SPECTROPHOTOMETER

INSTRUMENT NO. 2646334

E. I. DU PONT DE NEMOURS & CO.

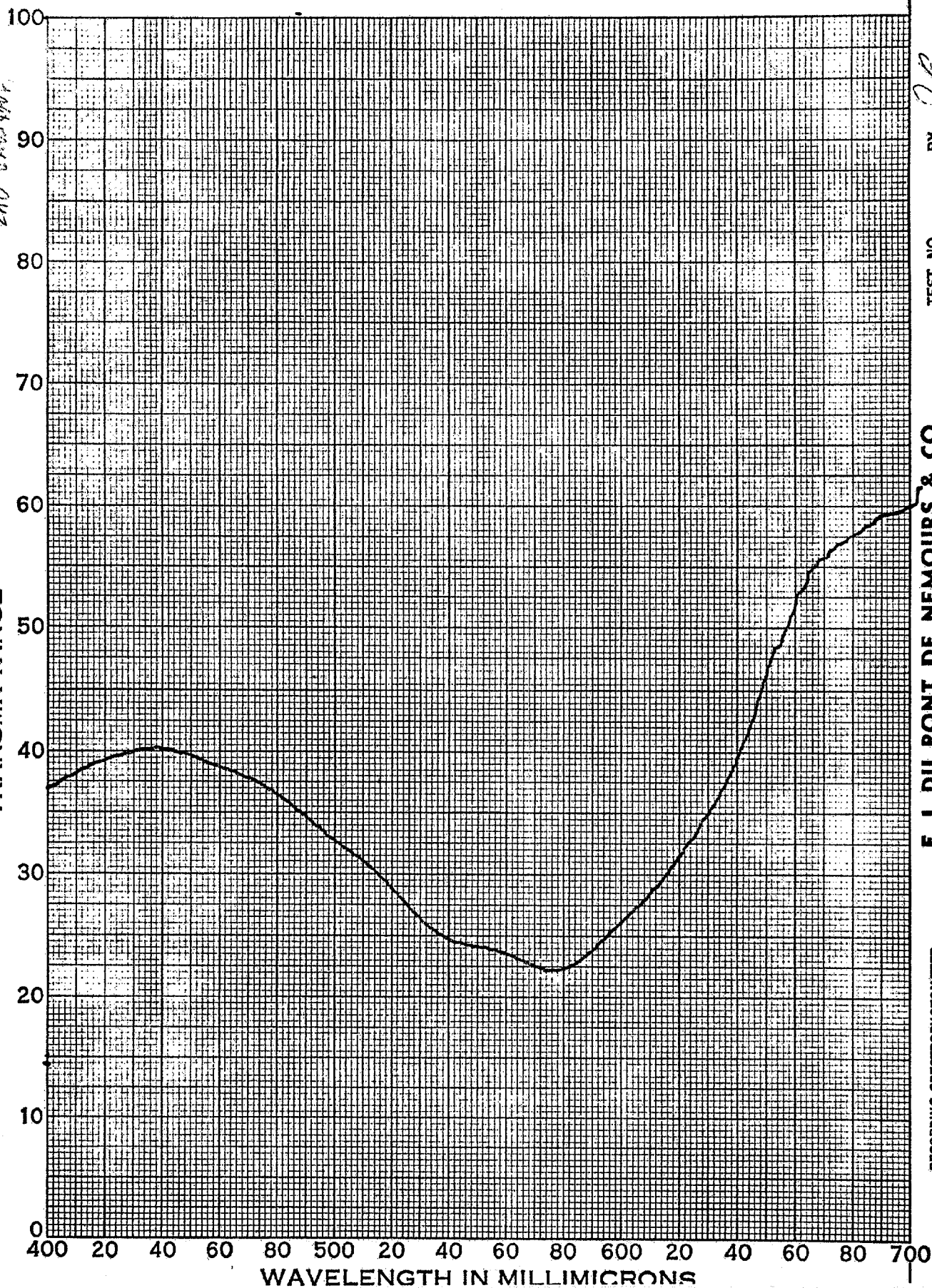
PIGMENTS DEPARTMENT

FOR ~~TESTING~~ LRL BY J.A.

DATE 11-15-68

1897-15B PC
2nd character

REFLECTANCE
TRANSMITTANCE (PERCENT)



E. I. DU PONT DE NEMOURS & CO.
PIGMENTS DEPARTMENT

RECORDING SPECTROPHOTOMETER

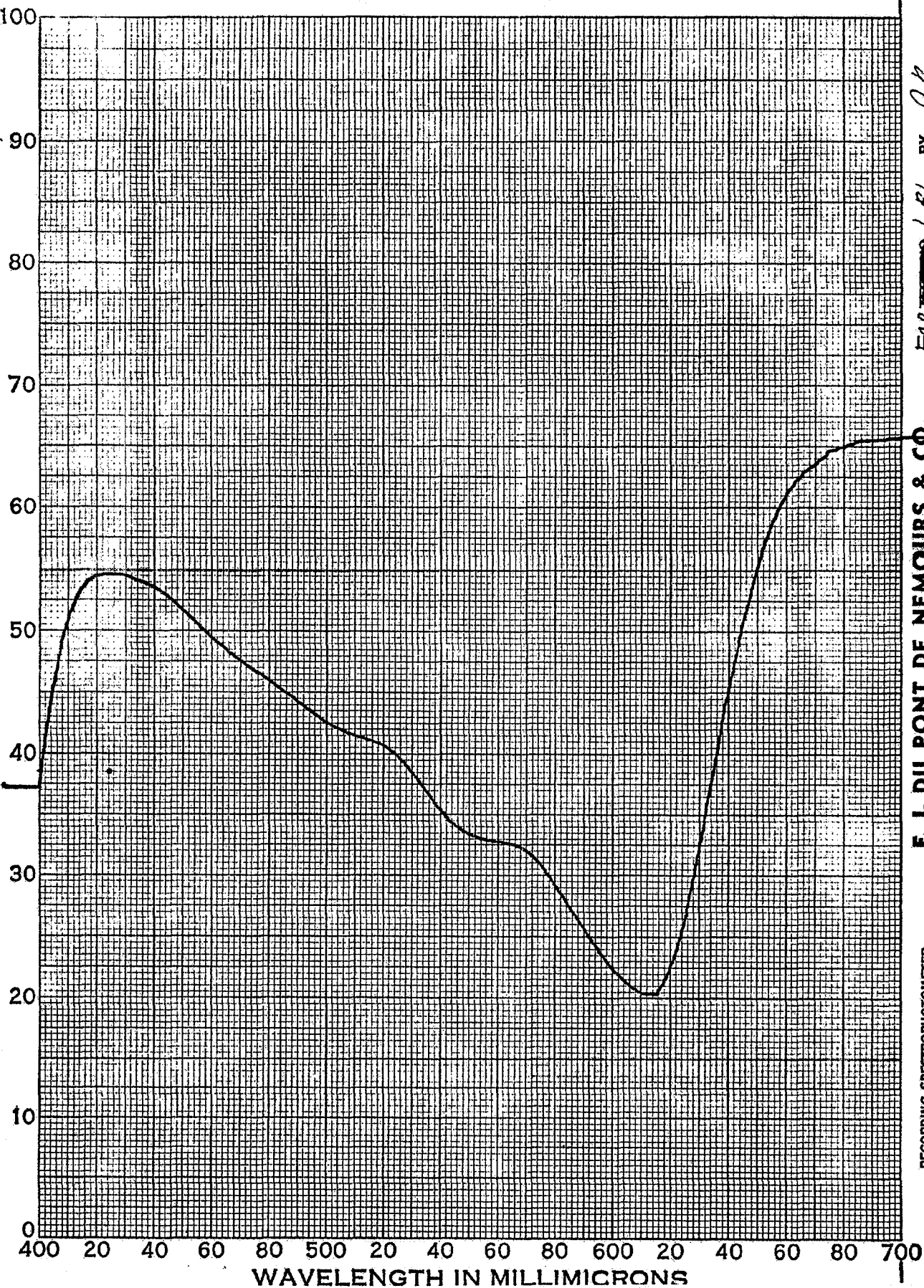
INSTRUMENT NO. 2646334

TEST NO. BY 22
DATE 10-28-65

68-744A 1297-32-1
Acrylic Lucite 5/95 Tim

2.0. Spectrophotometer 0.8" (1.5 mm)

REFLECTANCE
TRANSMITTANCE (PERCENT)



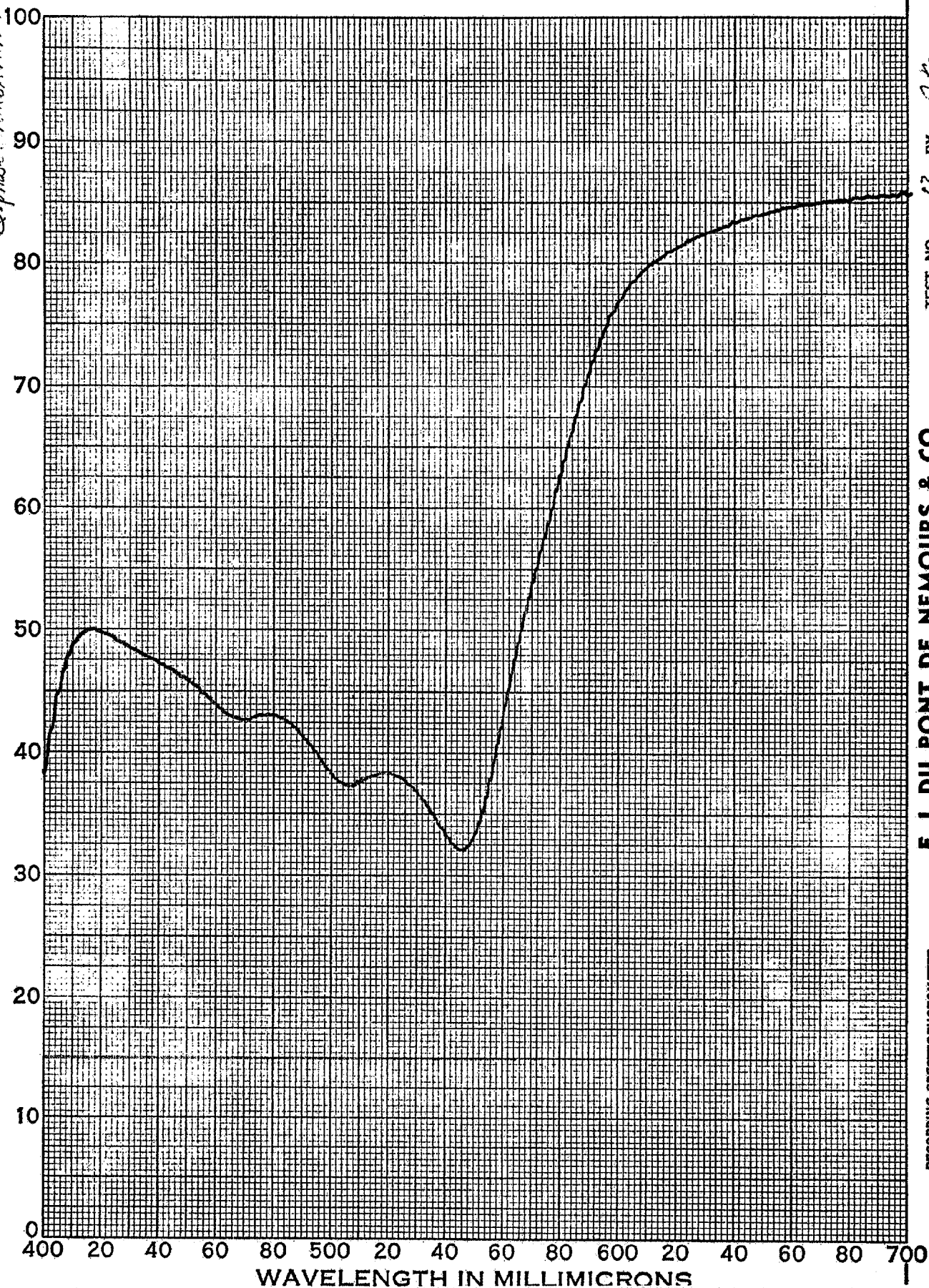
FOR RECORDING LRL BY J.R.
DATE 11-15-68

E. I. DU PONT DE NEMOURS & CO.
PIGMENTS DEPARTMENT

RECORDING SPECTROPHOTOMETER
INSTRUMENT NO. 2646334

1797-40C Orange-red
CRUDE 27-41 HOSOP 7A
De-phase (P. 10/10/10)

REFLECTANCE
TRANSMITTANCE (PERCENT)

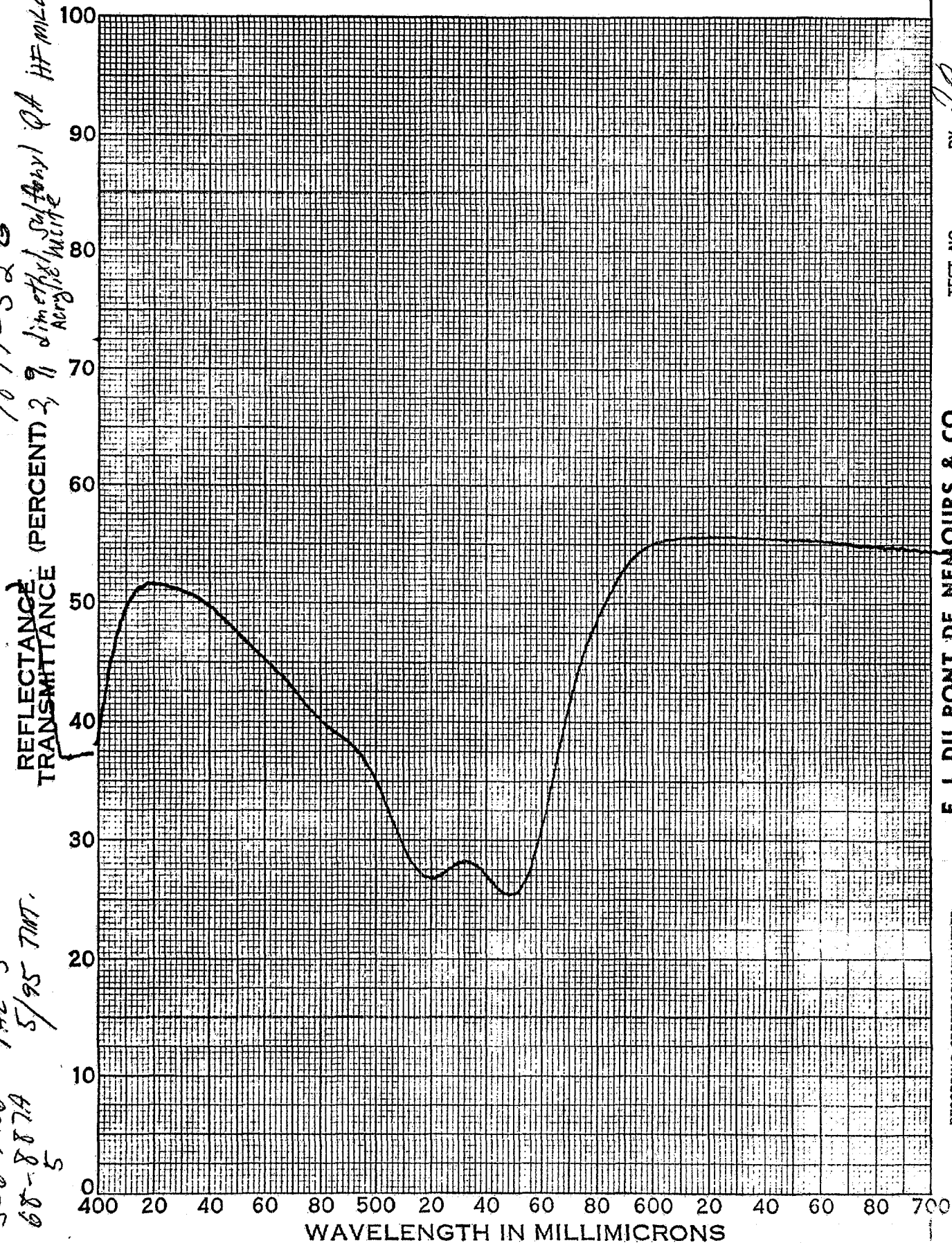


E. I. DU PONT DE NEMOURS & CO.
PIGMENTS DEPARTMENT

RECORDING SPECTROPHOTOMETER
INSTRUMENT NO. 2646334

TEST NO. 13 BY JH.
DATE 1-4-69

5-6 9406 TAE-3
 68-887A 5/95 TMT.
 1897-52 G
 9 Dimethyl Sulfate
 Acrylate Milled
 Q.A. HF MILLED



RECORDING SPECTROPHOTOMETER

INSTRUMENT NO. 2646334

E. I. DU PONT DE NEMOURS & CO.

PIGMENTS DEPARTMENT

TEST NO. BY *dlp*

DATE 11-31-53

1897-13 B-1 (very dark blue)
HF MILLED 2,3,9,10-tetraol GA
100% (very dark)

REFLECTANCE (PERCENT)
TRANSMITTANCE

100

90

80

70

60

50

40

30

20

10

0

400

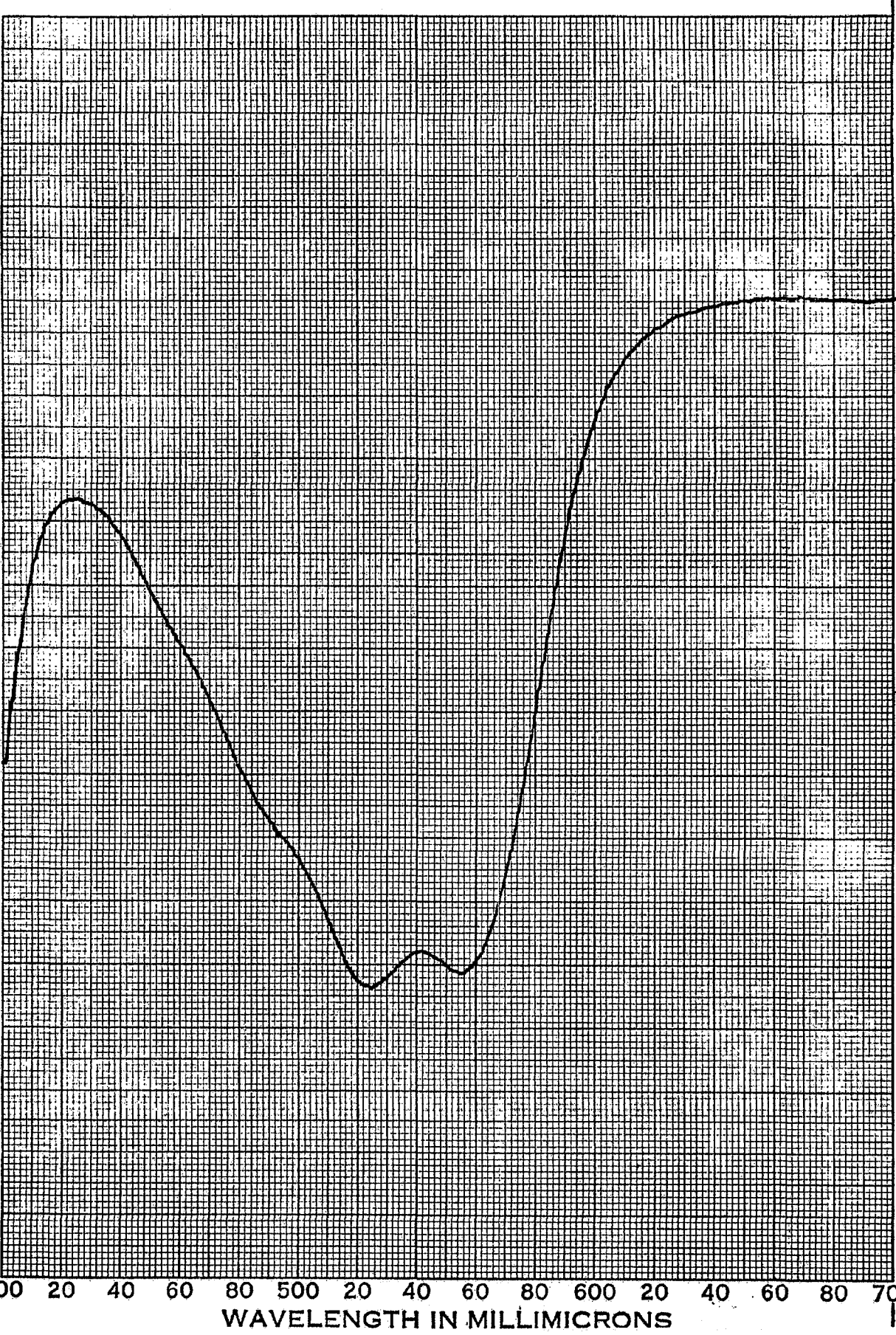
20

40

60

80

100



WAVELENGTH IN MILLIMICRONS

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PIGMENTS DEPARTMENT

RECORDING SPECTROPHOTOMETER

INSTRUMENT NO. 2846334

TEST NO. 13 BY JH.

DATE 1-24-69

APPENDIX II
X-RAY DIFFRACTION

1897-38

8-4-0-8-2

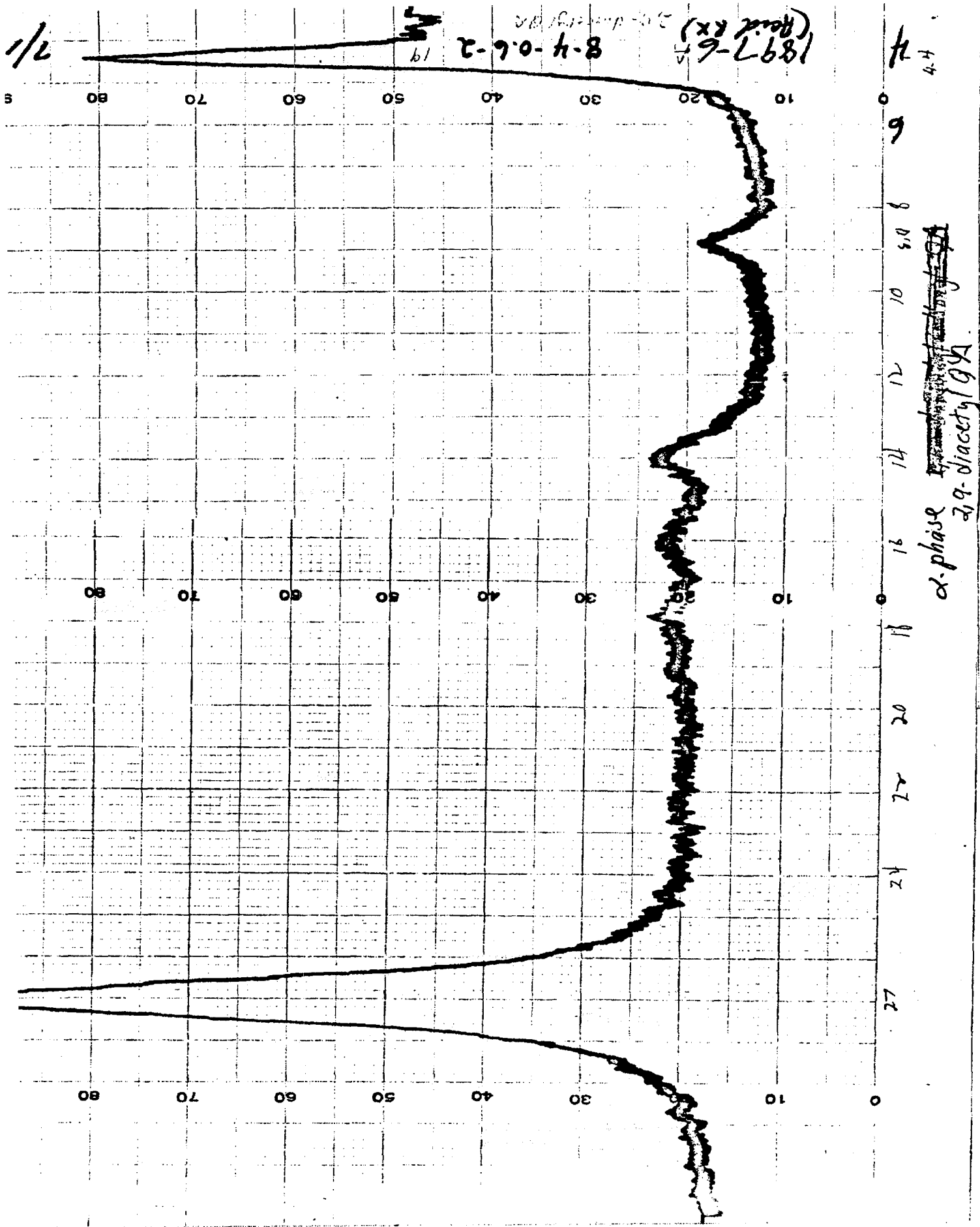
10/10/68

2-1-diacetamide GA 6hr DMF ref

10 20 30 40 50 60 70 80 90

10 20 30 40 50 60 70 80 90

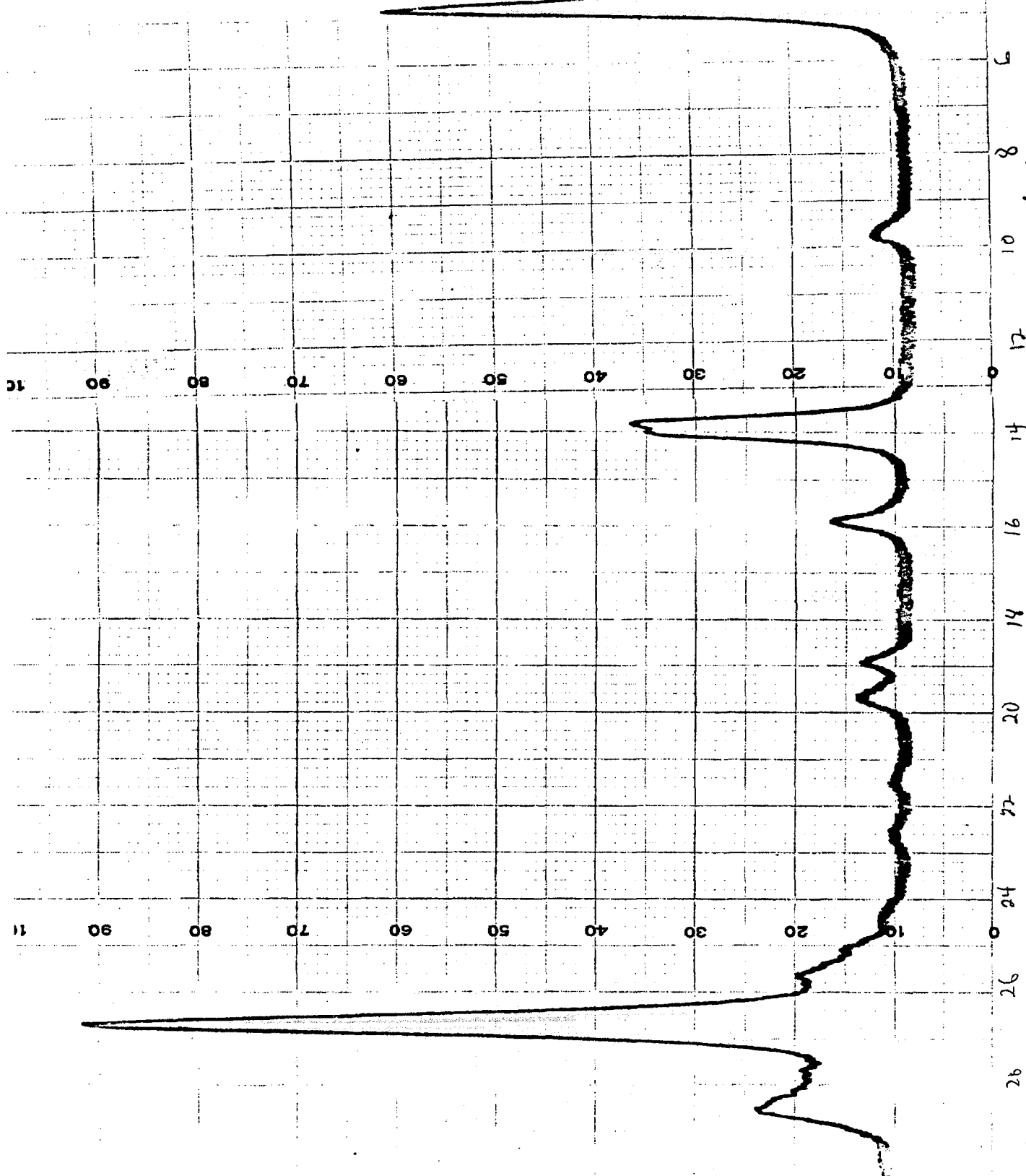
DUP050081961



1897-39
3,9-diacetyl GA - 8m DMF solution
8-8-8-2

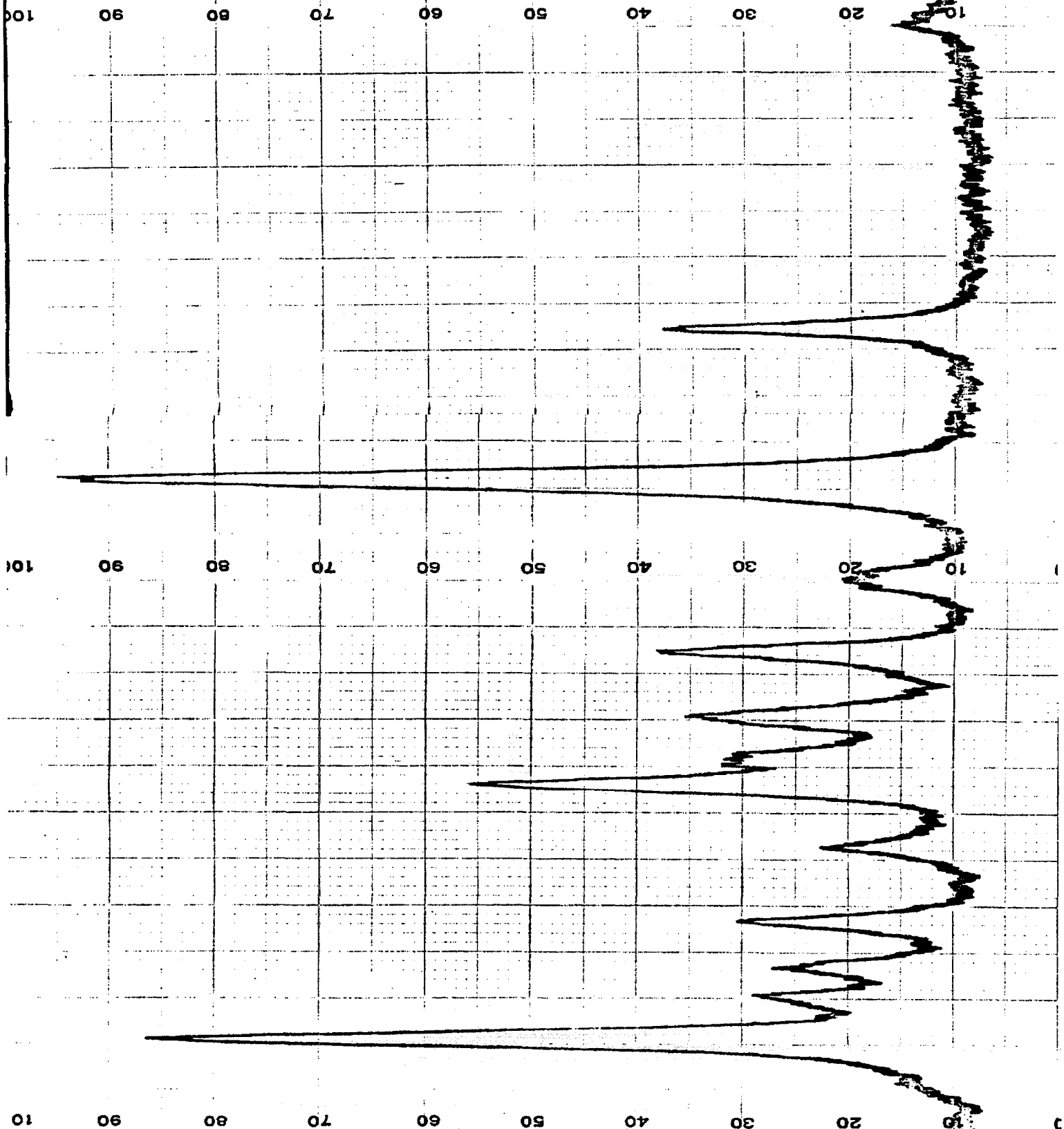
10/10/68 W

3-4
β-phase 3,9-diacetyl GA



1897-52F 8-2-0.6-2 241 DMF reflux 2,9-dimethylguanine (90)

12/17/82

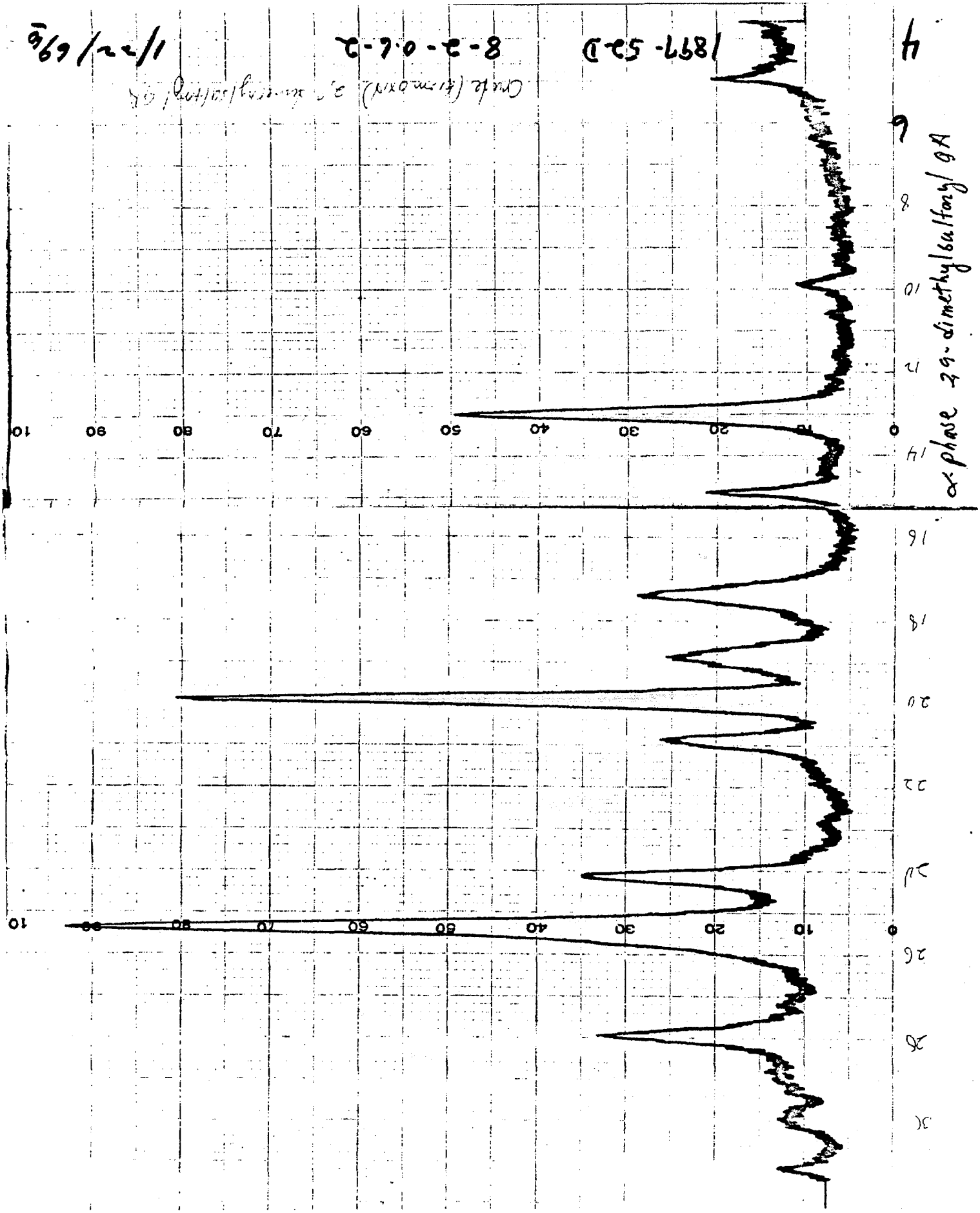


1/22/69

8-2-0-6-2

1897-52D

Crude (Kimmox) 3.5% dimethylbutyl 9A



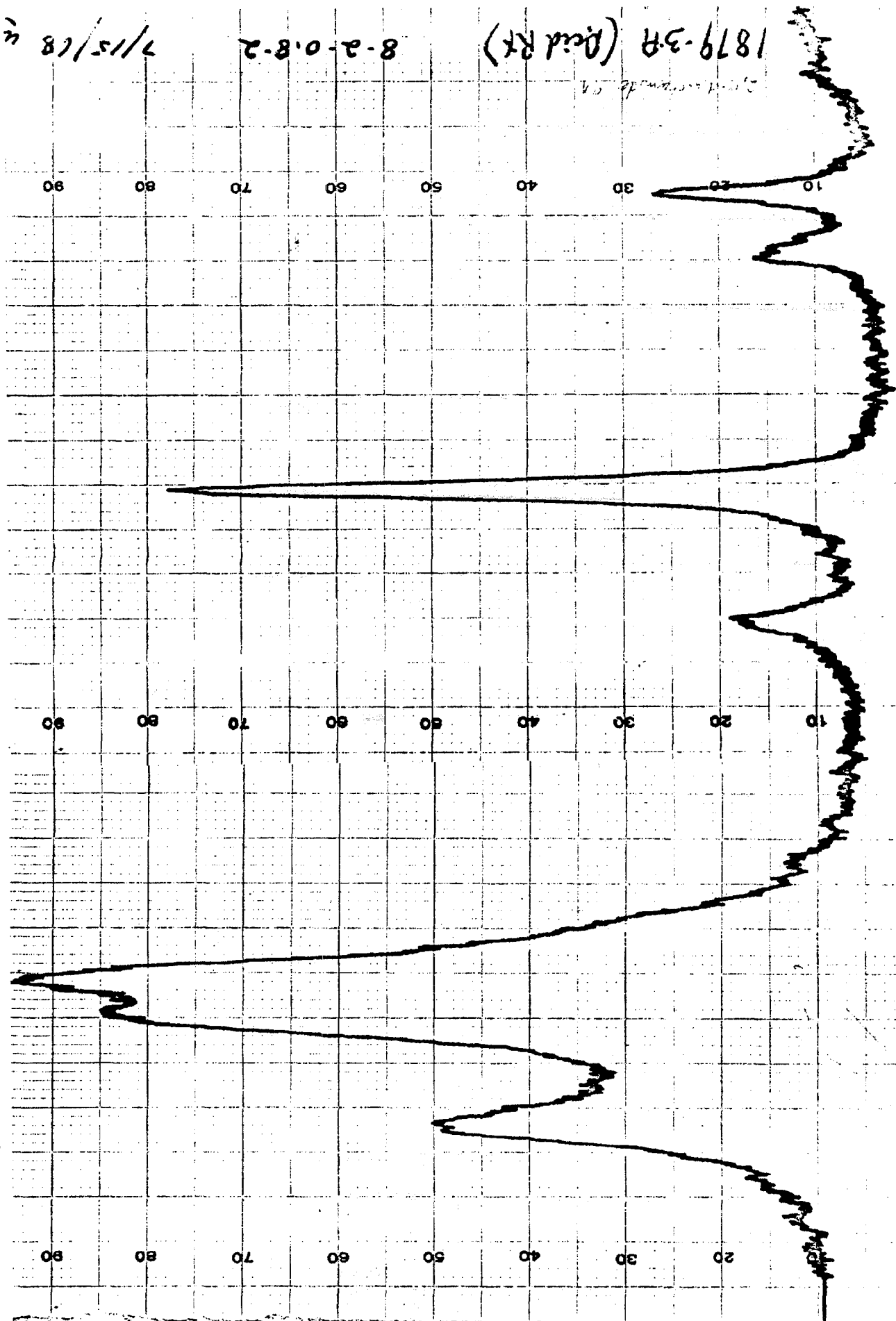
14 6 8 10 12 14 16 18 20 22 24 26 28 30

2-phase 29-diacetamido 7A

1879-3A (Acid Rx)

8-a-0.8-2

7/15/68 u



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