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DOW CHEMICAL U.S.A.

An Operating Unit of The Dow Chemical Company

WALNUT CREEK, CALIFORNIA

FINAL REPORT

Synthesis of Optically Clear Polymeric Materials for High Temperature Windows

Contract No. NAS2-6388

Submitted to:

National Aeronautics and Space Administration
Ames Research Center

March 1, 1971 - February 28, 1973

Submitted by: Dow Chemical U.S.A.
Western Division Research Laboratories
Walnut Creek, California

Principal Investigator: C. E. Pannell

Written by: C. E. Pannell and J. E. Magner

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FORWARD

This report covers work accomplished under NASA Contract NAS 2-6388. The goal of this contract was to synthesize and fabricate an optically clear polymer suitable for high temperature service. The work period was March 1, 1971 through February 28, 1973.

Dow Chemical Company personnel involved in the actual contract work were the following:

C. E. Pannell - Principal Investigator
J. E. Magner - Project Engineer
R. W. Mah - Project Chemist
B. Masuda - Project Chemist
T. L. Mincey - Project Technician

The NASA Project Monitor was Dr. G. M. Fohlen.

SUMMARY

A polymer has been developed that has excellent potential for use as windows in spacecraft as well as conventional aircraft. This polymer, phenolphthalein polycarbonate, has outstanding thermal properties, e.g., in place of melting or burning, it produces an insulating charred foam that closes off transmission of radiant heat through the window. This fact, coupled with an oxygen index of 0.43 and a 177°C (350°F) tensile strength of 58 mega Newtons/meter^2 (8400 psi), makes this polymer a prime candidate for further development. Pilot plant preparation in a 20 gallon Pfaudler kettle was accomplished and large test specimens were prepared for NASA evaluations.

PROGRAM GOALS

The objective of this program was the development of a thermally stable optically clear polymer suitable for use as windows in aircraft and aerospace vehicles. The specific work objectives were to prepare, characterize and supply candidate polymers to NASA personnel for evaluation. The desired polymer was to have the following properties.

A. Be optically clear and colorless.

B. Have thermal integrity, including a Tg (glass transition temperature) of at least 250°C.

C. Have characteristics of an ablative heat shield.

D. Have a high impact strength.

E. Be non-flammable.

F. Be easily processable.

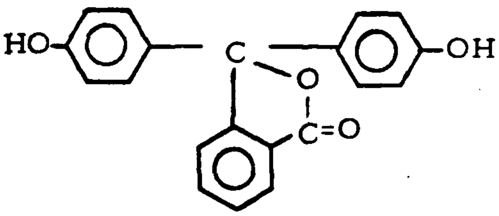
The contract was to involve a three-phase work sequence leading to a candidate which would be chosen on the basis of NASA evaluation. The chosen candidate would then be further characterized by an extensive NASA testing program requiring an adequate polymer supply as well as fabrication into suitable test samples. The extensive testing program and attendant polymer supply and sample fabrication were not a formal part of the initial contract; however, the program was broadened by a contract extension to include these areas.

Phase	Work Plan	Work Goal	Program Decision
I	Synthesis and characterization of homopolymers	NASA evaluation to choose candidates	1. Initiate Phase II 2. Optimize chosen polymer for second stage
II	Copolymerization of selected Phase I monomers	Optimize polymer properties to meet goals	1. Initiate Phase III 2. Optimize selected copolymer for second stage
III	Modification of selected copolymers by reactive materials	NASA evaluations to guide optimization	1. Optimize selected system for second stage work sequence
	- Second Stage -		
	Optimize polymer synthesis and fabrication methods	NASA evaluation of test specimens	Scale-up polymer synthesis and fabricate prototype windows

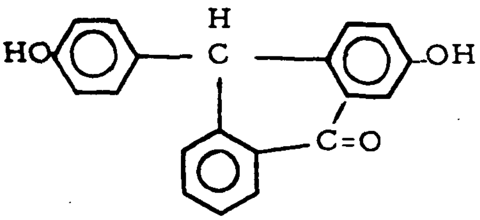
RESULTS

The contract work statement involved two definite stages with stage I calling for the preparation and characterization of eleven homopolymers. The monomers from which these polymers were to be prepared cover a wide range of structural types. The following monomers were included in stage I.

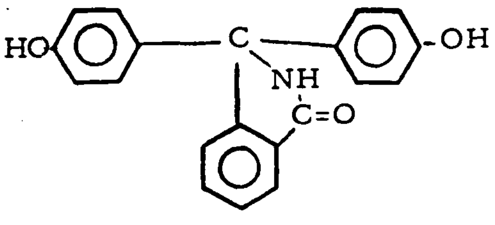
Stage I Monomers



1. Phenolphthalein

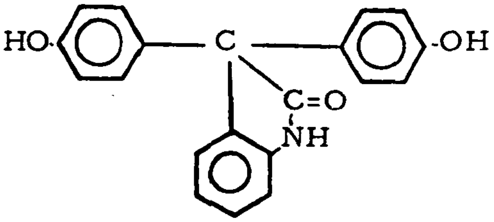


2. Phthalidin,
(2-hydroxy-10-(p-hydroxyphenyl)anthrone



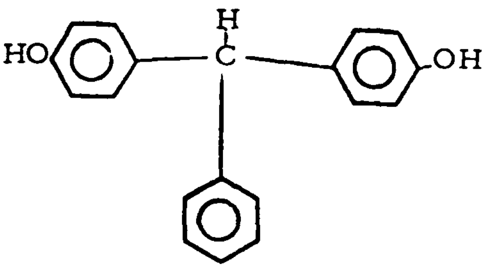
3. Phenolphthalimidine,

(3, 3-bis(4-hydroxyphenyl)-isooxindole

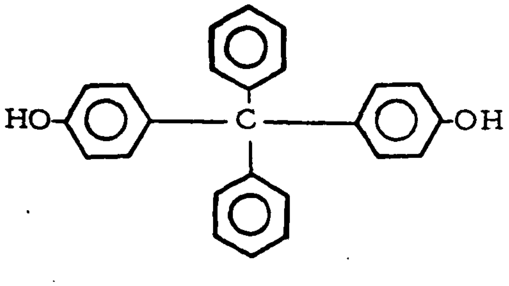


4. Phenolisatin,

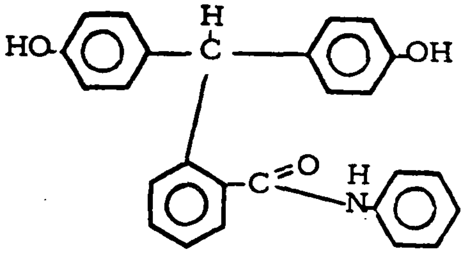
(3, 3-bis(4-hydroxyphenyl) oxindole



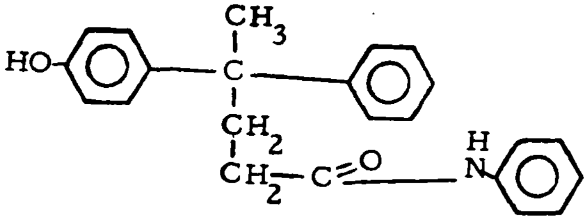
5. 4, 4'-Dihydroxytriphenylmethane



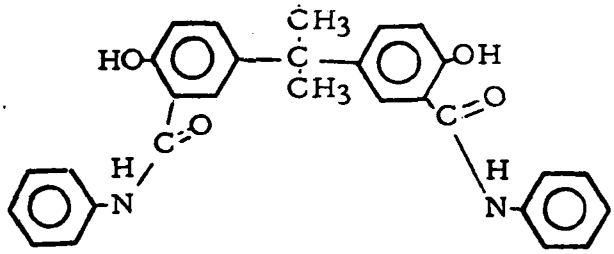
6. 4, 4'-Dihydroxy tetraphenyl methane



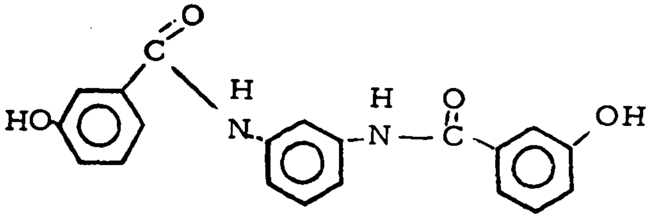
7. Phenolphthalin anilide



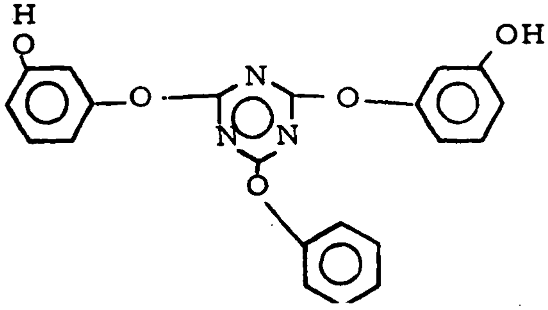
8. Diphenolic acid anilide



9. Anilide of Carboxylated Bisphenol Acetone



10. N, N'-m-Phenylene di-3-hydroxy-benzamide

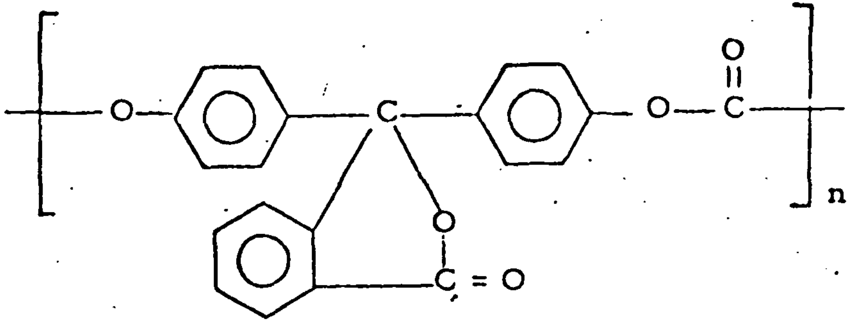


11. 2, 6-di(3-hydroxy phenoxy)-4-phenoxy 1, 3, 5-triazene

The first polymer submitted to NASA personnel was the phenolphthalein polycarbonate (PPR Resin) based upon Structure 1, and the NASA evaluation of this polymer established that it had an excellent chance of meeting the contract goals. The general properties of the phenolphthalein polymer are presented in the following table.

Properties of Phenolphthalein Polycarbonate

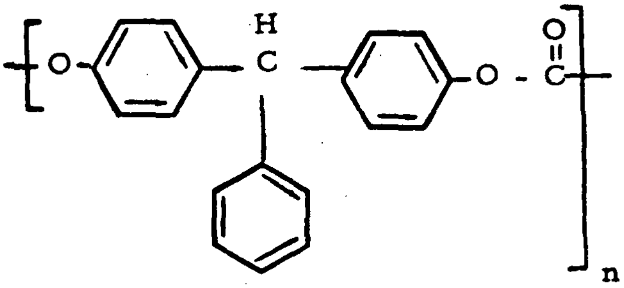
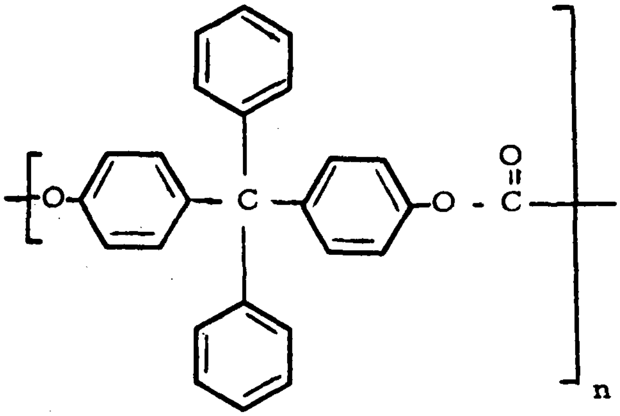
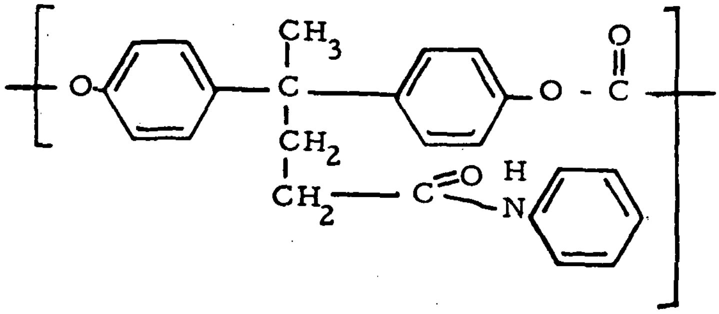
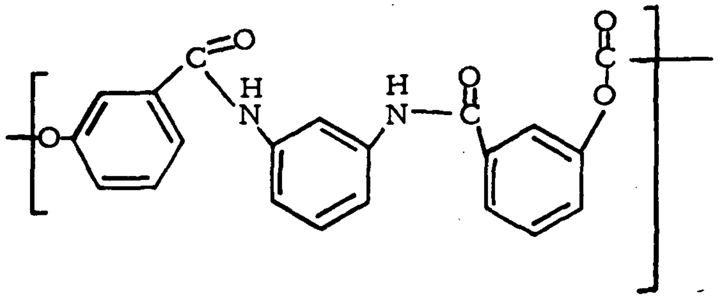
Structure



Molecular Weight	Up to 200,000 Inherent viscosities up to 2.5 (0.5% solution)
Color	Films have been prepared that were clear and colorless
Stability	Hydrolyzed by Bases Decomposes ~425°C (<1% wt. loss by 400°C) (TGA in air)
Physical Properties	Glass Transition Temperatures 275°C Heat Distortion Temperature 240-5°C Tensile 25°C - 15,000 psi (103 MN/m^2) 150°C - 9,000 psi (62 MN/m^2) 260°C - 3,600 psi (25 MN/m^2) Young's Modulus - 365 - 400,000 psi at 25°C (2.6 - 2.8 GN/m^2) Specific Gravity - 1.335 Water absorption (1-2 mil film) 0.7 - 0.9% (24 hr.soak) Oxygen Index - 0.43 Chars and Intumesces without melting under propane torch Pencil Hardness - 6-7H (Lexan 1H, Lucite 8H) Barcol Hardness - 86 (Lexan 70, Lucite 90) Flexural Strength - 22,000 psi at 25°C (152 MN/m^2)

The superior properties of the phenolphthalein polymer resulted in a decision by NASA to shift to second stage research; hence only four other homopolymers were delivered to NASA for examination. The following table lists these polymers.

Additional Stage I Homopolymers Delivered to NASA

Structure	Inh. Vis. (0.5%)	Glass Transit. Temp. °C	Polymer Melt Temp. °C
	0.68 (in CH_2Cl_2)	181°	220°
	0.64 (in CH_2Cl_2)	213°	260°
	0.59 (in DMF)	164° (cryst. mp)	190°
	0.22 (in DMF)	260° (cryst. mp)	310° (dec)

The second stage of the program had the following objectives:

A. Fabrication and tensile testing of small specimens.

B. Synthesis of an adequate quantity of polymer.

C. Fabrication of large test panels for NASA evaluation.

The tensile data obtained from the small test specimens is presented in the table below.

TENSILE PROPERTIES OF PHENOLPHTHALEIN POLYCARBONATE

PPR Polymer Prep. Number	Sample No.	Thickness in. (mm)	Width in. (mm)	Temp. °C	Max. Tensile[c] psi (MN/m^2)	Elon. %	Modulus psi (GN/m^2)
195A	a	0.113 (2.87)	0.161 (4.09)	25°C	17,000 (122)	14	335,000 (2.31)
195A	b	0.104 (2.64)	0.150 (3.81)	150°C	7,050 (48.6)	46	---
195A	c	0.101 (2.57)	0.148 (3.76)	150°C	7,358[d] (50.9)	78	---
195	d	0.066 (1.68)	0.165 (4.19)	25°C	12,100 (83.4)	5	---

NASA Determinations

PPR Polymer Prep. Number	Sample No.	Temp. °F (°C)	Yield[c] psi (MN/m^2)	Break psi (MN/m^2)	Modulus psi (GN/m^2)
195A	1	RT	13,285 (91.6)	8,950 (61.7)	146,626 (1.01)
	2	200 (93)	11,319 (78.0)	8,002 (55.2)	194,891 (1.34)
	3	350 (177)	8,428 (57.9)	---	180,817 (1.25)
195B	6	RT	13,122 (90.5)	7,645 (52.7)	156,313 (1.08)
	7	100 (38)	---	12,656 (87.6)	181,743 (1.25)
	8	150 (66)	11,814 (81.5)	---	174,594 (1.20)
	9	200 (93)	10,816 (74.6)	---	145,212 (1.00)
	10	250 (121)	9,237 (63.5)	---	169,429 (1.17)
	11	300 (149)	8,730 (60.2)	---	169,101 (1.17)
	12	350 (177)	6,889 (47.5)	---	155,530 (1.07)
195C	16	RT	---	10,281 (70.9)	193,195 (1.33)
	17	200 (93°C)	10,455 (72.1)	7,658 (52.8)	218,740 (1.51)
	18	350 (177°C)	7,646 (57.7)	---	217,895 (1.50)

(a) Scatter was observed due to the fact that the microtensile specimens were punched from a 0.1" sheet ASTM procedure specified milling to avoid flaws that result from a punching or stamping process.

(b) PPR Prep. No.: 195A - inherent visc. 1.37; 195B - inherent visc. 1.08; 195C - inherent visc. 0.59.

(c) Instron crosshead speed 0.01 inches/minute (0.254 mm/min.)

(d) Sample slipped in grips several times before failure.

(e) Instron crosshead speed 0.1 inches/minute (2.54 mm/min).

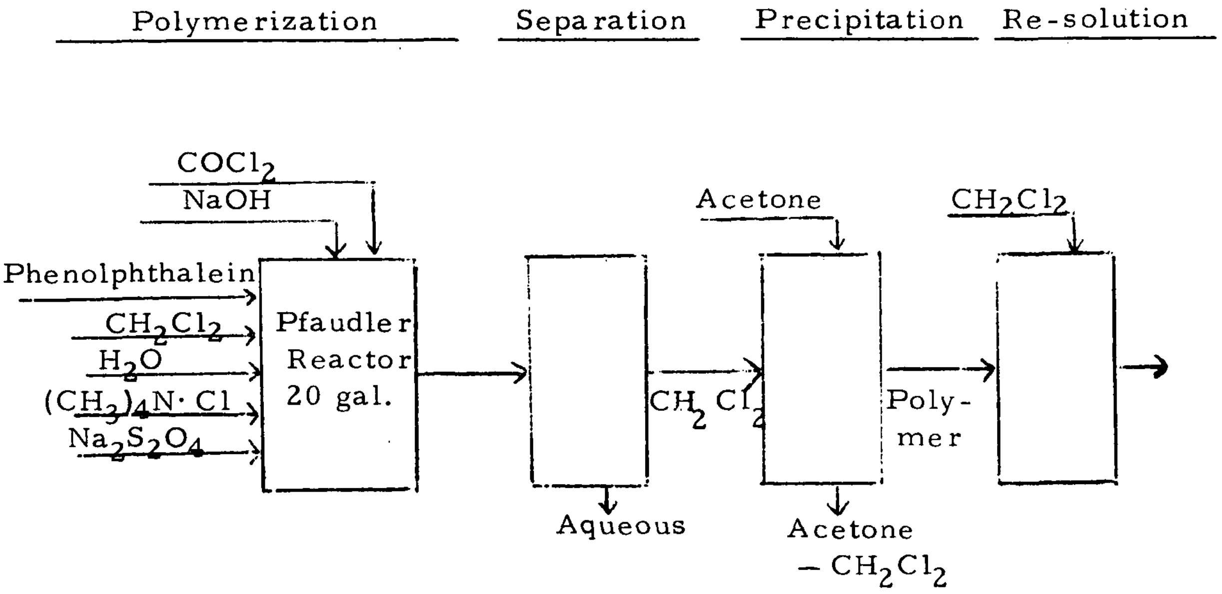
This tensile data was preliminary and needed verifying; accordingly, the expedient preparation of pilot plant quantities of polymer was accomplished. This polymer was then fabricated into 8" x 10" x 1/8" test panels.

The pilot plant preparation (20 gallon Pfaudler Kettle) is discussed later. A successful laboratory preparation was used and no process work (such as ascertaining the parameters that control the molecular weight and optimum procedures for polymer isolation) was done.

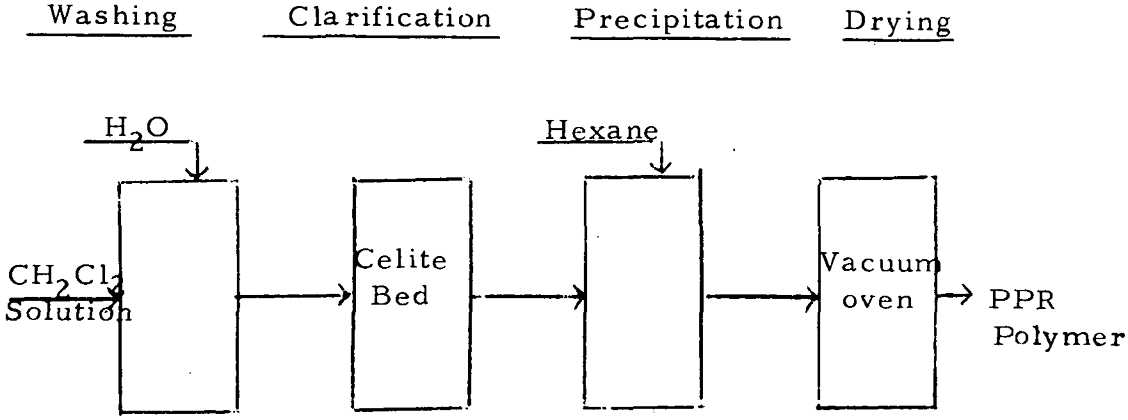
Pilot Plant

The polymerization was accomplished using a 20 gallon Pfaudler Kettle. A block diagram is as follows:

PILOT SCALE PRODUCTION OF PPR



Pilot Scale Production of PPR cont.

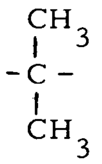
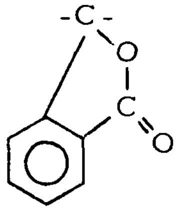


Large Panel Fabrication

The fabrication method chosen was the same as that chosen for the preliminary fabrications, and involved the use of a fugitive plasticizer, either dichloromethane and/or acetone. This unorthodox approach failed to yield consistent optical quality specimens; hence it was decided not to determine optical properties.

The evaluation by NASA personnel indicated that these materials have glass transition temperatures of nearly 280 °C and a thermogravimetric char yield of about 54%. Moldings of the neat polycarbonate have initial tensile strengths at room temperature of about 110 to 138 MN/m^2 and retain as much as 41.4 MN/m^2 at 200°C.

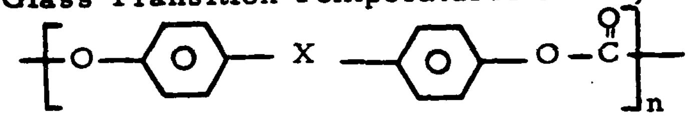
Effect of Monomer Structure on the Thermal Properties of Aromatic Polycarbonates. (Determined in N_2)

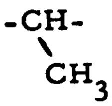
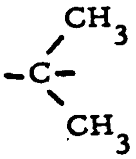
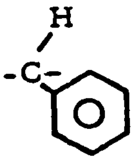
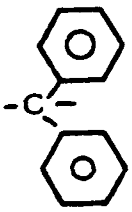
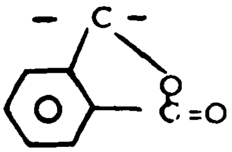
Polycarbonate Type, -R-	T_g, °C	T_m, °C	T_d, °C	$Y_C^{800^\circ}$, %
Bisphenol A  $-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-$	150	190	400	20
Phenolphthalein 	278	295* *softens	425	54

DISCUSSION OF RESULTS

The program objectives required the development of an optically clear plastic having exceptional thermal properties and a high glass transition temperature. One means of obtaining a high glass transition temperature is to introduce rigid chain stiffening segments in the polymer backbone. Phenolphthalein is a rigid monomer and the following table illustrates the influence of rigid chain stiffening groups when incorporated into a polymer.

Glass Transition Temperatures of Polycarbonates

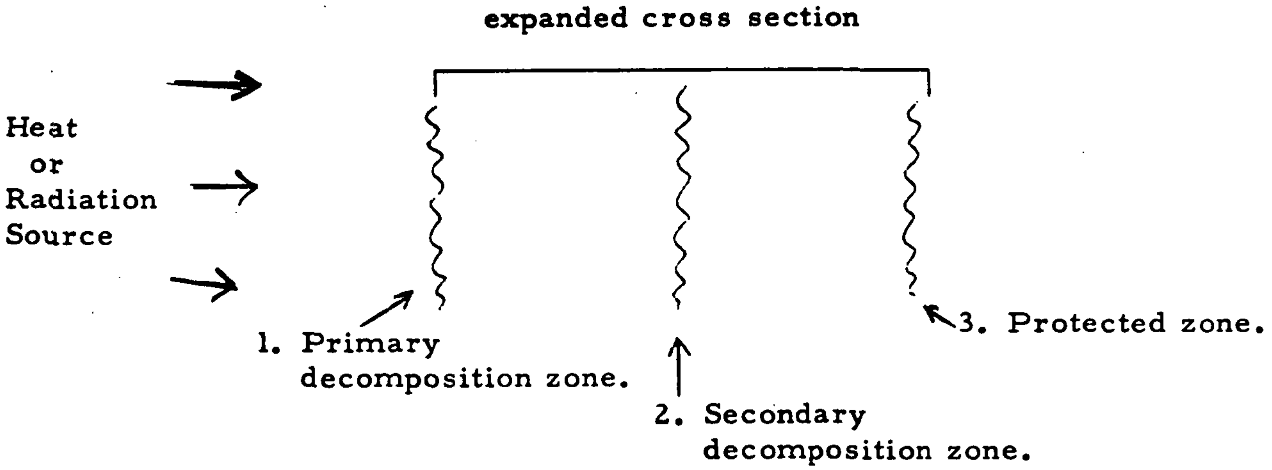


X	T_g °C
$-CH_2-$	melts >300° - unrestricted chain rotation permits crystallization
 $-CH(CH_3)-$	130°
 $-C(CH_3)_2-$	149°
	180°
	213°
	275°

A desirable feature displayed by the PPR polymer is that thermal decomposition produces a foam that effectively turns the specimen opaque, thus shutting off transmission of heat radiation through the window.

The non-burning characteristics of the polymer, coupled with the ablative and charring properties, make the polymer worthy of further development. The oxygen index of 0.43 is very significant since halogen and its resulting corrosive gasses would be absent.

Mass spectral examination of the polymer reveals that the initial stages of decomposition involve loss of CO_2, presumable via chain cleavage. Subsequent decomposition involves degradation of phenolphthalein into CO_2 as well as ring moieties such as phenol and benzene. It is presumably this initial CO_2 release that is responsible for the excellent thermal behavior of the polymer. A possible model is as follows:



1. **Primary zone (boundary surface). Initially foamed by CO_2 release followed by char formation on continued heating.**

   Polymer $\xrightarrow[400-450°]{\Delta}$ CO_2 + polymer fragments $\xrightarrow{\Delta}$ CO_2 + decomposition products + char (temp determined by TGA behavior).

2. **Secondary zone. Turned opaque via CO_2 loss. Further decomposition dependent upon intensity and duration of radiation.**

3. **Protected zone. Insulated by neighboring opaque foamed layer.**

Extensive NASA investigations indicate that an integral feature of this system involves thermally induced cross-linking resulting in a high char yield and excellent ablative properties.

CONCLUSIONS AND RECOMMENDATIONS

The synthesis of large transparent panels from phenolphthalein polycarbonate has been accomplished. Evaluation of the fabricated specimens by NASA personnel has established that the polymer has outstanding thermal resistance.

These features coupled with the transparency results in the polymer being an excellent candidate for window use in aircraft enclosures as well as space craft.

Continued work is recommended involving the following:

A. Process Development

  a. Optimize Polymer Properties

  b. Establish Processing Parameters

B. Product Development

   a. Chemical Property Analysis

   b. Physical Property Analysis

Only by undertaking a program of this sort will the necessary data be obtained to permit proper assessment of the phenolphthalein polycarbonate potential.

Reliable mechanical property data is obtained only as a result of an extensive program whereby numerous variables have been firmly brought into control. With Lexan, a commercial polycarbonate, as a guide, there are at least five properties that are particularly sensitive to either synthesis or processing variables. They are:

1. Optical properties

2. Color

3. Tensile strength

4. Impact strength

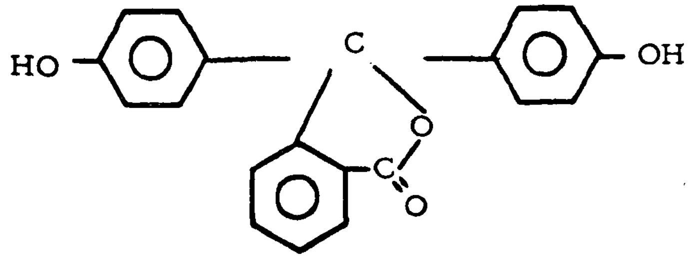
5. Processability

The contract time remaining ruled out an extensive study of this nature, accordingly, the large test panels (8" x 10") were fabricated in the same manner as the preliminary test specimens. The fugitive plasticization method for preparation of the test panels was used because high temperature compression moldings furnished partially fused samples that were discolored and degraded. Further work involving process improvement with particular emphasis upon isolation and purification techniques could eliminate this undesirable polymer behavior at elevated processing temperatures.

EXPERIMENTAL

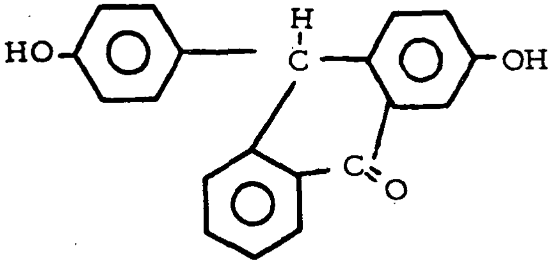
Monomer Preparation

1. Phenolphthalein

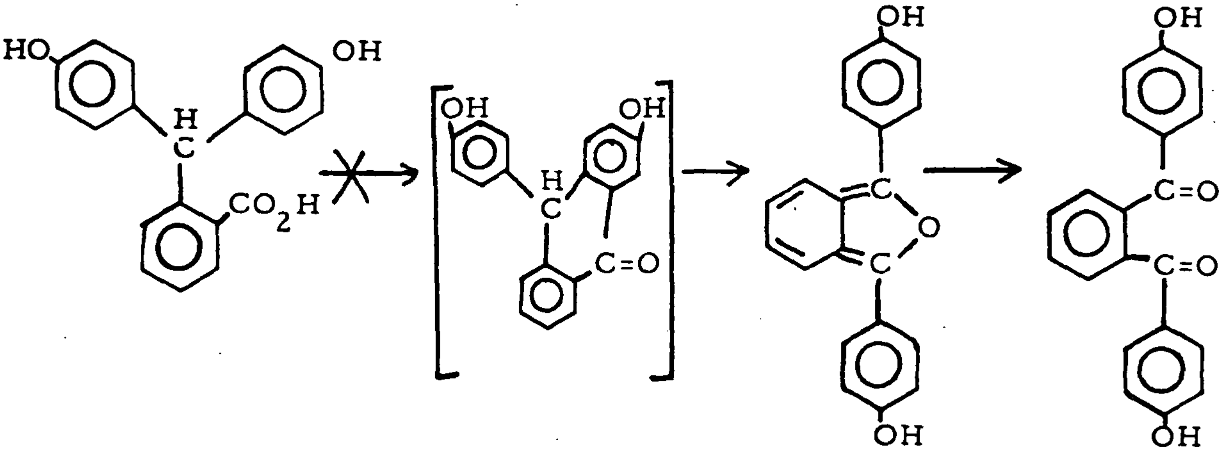


This monomer was purchased. The ACS reagent grade was of adequate polymer grade purity to be used without further purification. An excellent preparative procedure can be found in Vogel[1] Appendix 1 presents the DTA melting behavior and IR spectra.

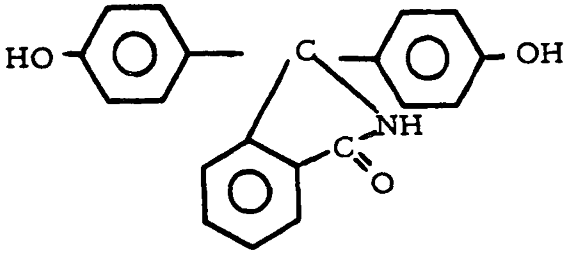
2. Phthalidin, (2-hydroxy-10-(p-hydroxyphenyl) anthrone



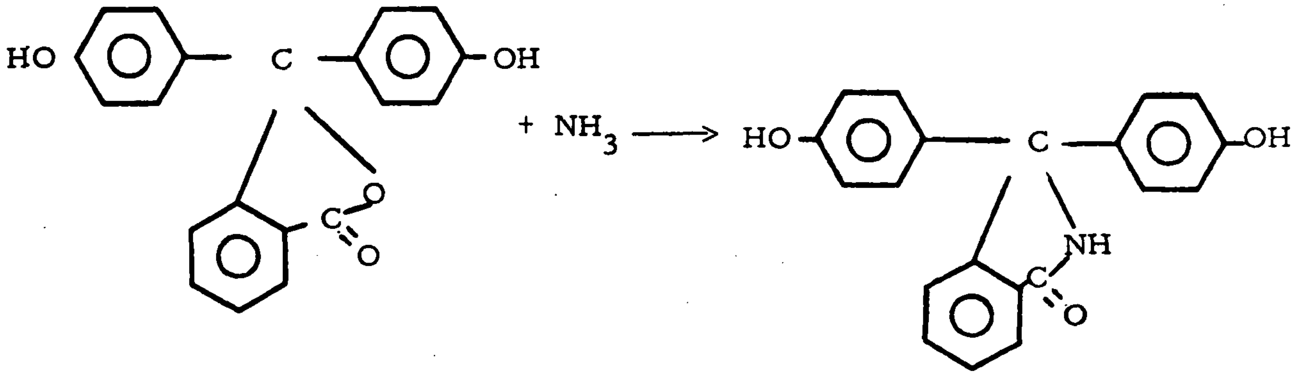
This monomer was not prepared. The proposed route to the compound was based upon a reaction published by Baeyer[2] in 1880. Later research by Blincke[3] established that the reaction did not yield the desired compound. No actual work was devoted to this monomer.



3. Phenolphthalimidine, (3,3-bis(4-hydroxyphenyl)-isooxindole
(Reference GW 3-68:106)



This was prepared from phenolphthalein and ammonia. An excellent literature reference concerning the preparation can be found in a Ciba patent[4].



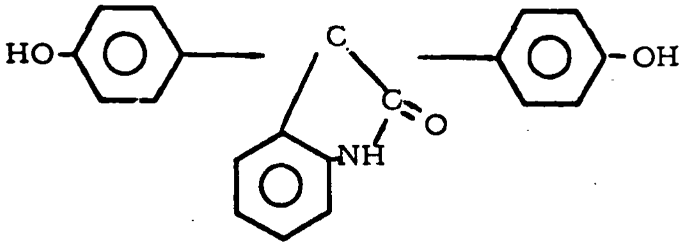
Procedure:

100 g of phenolphthalein was dissolved in one liter of 28% aqueous ammonia and allowed to stand for seven days at room temperature. The color at this time had faded to a dull claret. Agitation caused crystallization. The entire mass was poured onto conc. HCl and ice and the solid was collected and washed. The dried material melted at 283-284° and weighed 97 g. IR scan in Appendix I.

Anal. calc. for $C_{20}H_{15}NO_3$

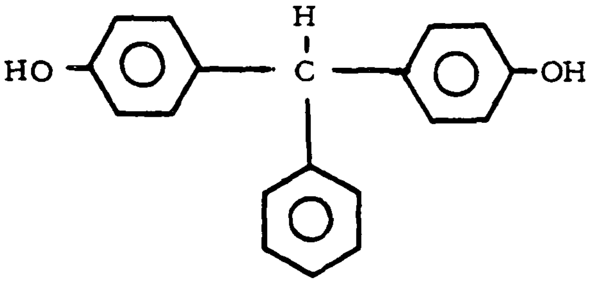
Calc.:		Found:	
	C 76.9%		C 75.7%
	H 4.9		H 4.8
	N 4.3		N 4.4

4. Phenolisatin, (3,3-bis(4-hydroxyphenyl) oxindole

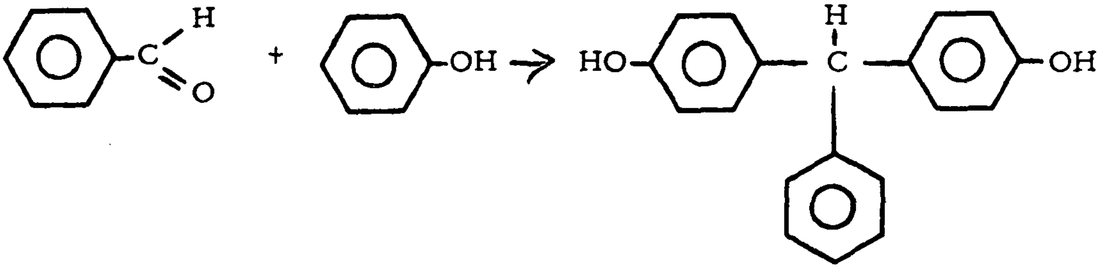


This material can be purchased. It was not studied. A preparative example can be found in a Ciba patent[4].

5. 4,4'-Dihydroxytriphenylmethane (Reference GW-3-68:107)



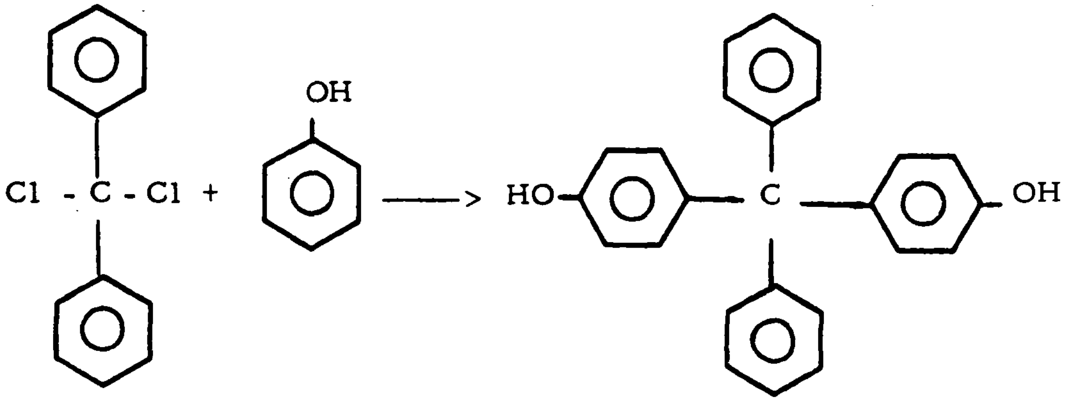
The preparation of this triphenyl compound was based upon acid catalyzed condensation of benzaldehyde and phenol. The procedure was essentially identical to a bis-phenol acetone preparation.



Procedure:

There was placed in a 2-liter flask 100 g of benzaldehyde, 500 ml of glacial acetic acid and 600 g of phenol. The solution was immersed in an ice bath and 100 ml of concentrated sulfuric acid dissolved in about 200 ml of glacial acetic acid was added. The solution was maintained at ~7°C for four days. At this time, water was added and the entire solution extracted with ether after which the ether was extracted with $NaHCO_3$ solution, followed by water washing. The ether was removed and then the excess phenol was removed using a rotating evaporator. The residue was then steam distilled, leaving a residue that was crystallized from an alcohol-water mixture. The dried product melted at 165-167°. Literature[5] records a 161° melting point. IR scan in Appendix I.

6. 4,4'-Dihydroxy tetraphenyl methane (Reference GW 50-70-74)

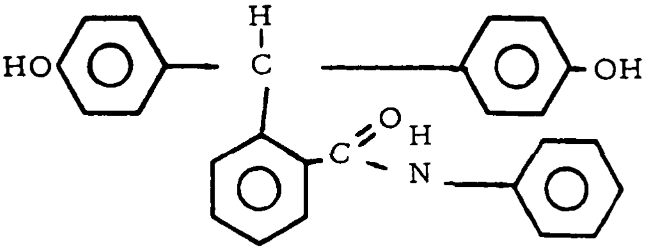


Phenol (66 g) was placed in a 200 ml flask and dichloro diphenylmethane (50 g) was added with efficient stirring. A vigorous HCl evolution accompanied the mixing. The flask and contents were then heated to 100°c. After four hours' stirring, the mass began to solidify and some THF was added to break up the solid cake forming. The slurry was then concentrated and the residue steam distilled. The non-volatile product was dissolved in caustic solution, ether extracted and the caustic solution is acidified and the solid filtered, and after washing was crystallized from ethanol. The dried product weighed 60 gms and melted at 291-292°. Literature[6, 6a] records a 295° melting point; IR scan in Appendix I.

Analysis Calc. for $C_{25}H_{20}O_2$

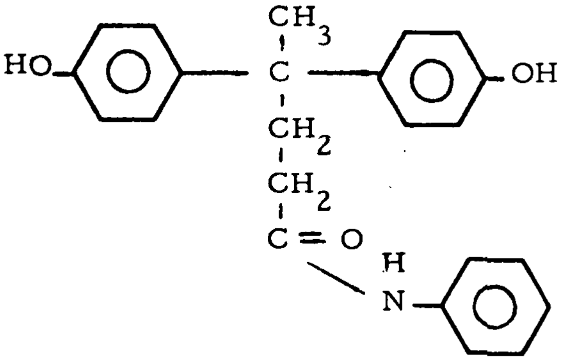
Calc:			Found:		
	C	85.3%		C	85.6%
	H	5.7		H	6.0

7. Phenolphthalin anilide

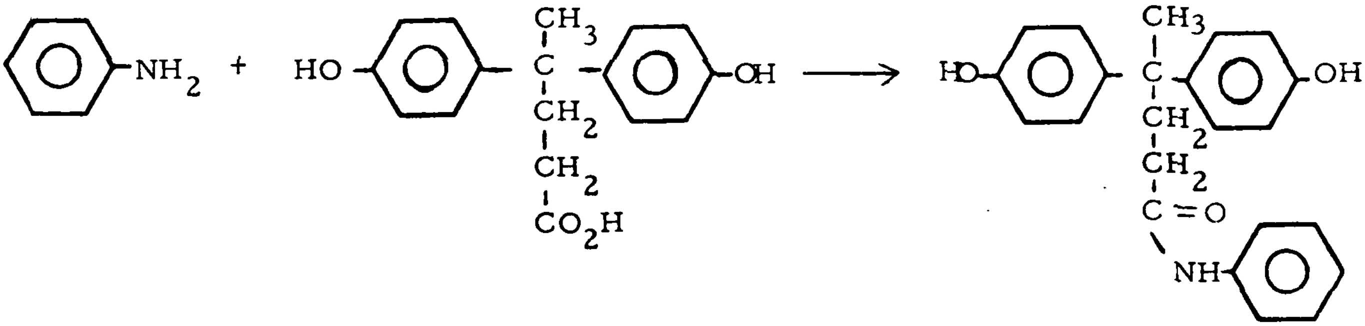


No work was done on preparing this compound. The proposed route was to prepare the anilide of commercially available phenolphthalin.

8. Diphenolic acid anilide (Reference GW 3-68:109)



Preparation was accomplished by reacting aniline with commercially available diphenolic acid.



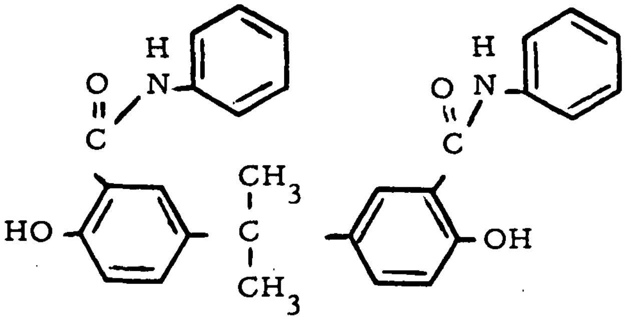
Procedure:

There was placed in a flask 150 ml of redistilled aniline and 57.2 g of diphenolic acid. This solution was heated at reflux under a nitrogen pad for 14 hours. A Dean-Stark trap was used to permit water removal. The excess aniline was vacuum stripped and the residue steam distilled to remove residual aniline. The residue was recrystallized from isopropyl alcohol-hexane misture yielding 39 g of a product that melted at 202-204°C. S. C. Johnson bulletin on diphenolic acid[7] gives directions for preparing this anilide. IR scan in Appendix I.

Analysis Calc. for $C_{23}H_{23}NO_3$

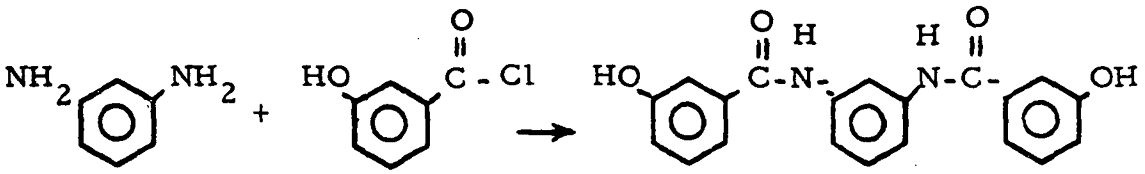
Calc:	C	76.43	Found:	77.1
	H	6.41		6.6
	N	3.88		3.8

9.



This material was not prepared. The proposed route was to involve carboxylation (Kolbe-Schmidt reaction) of bisphenol acetone, followed by conversion to the anilide.

10. N,N'-m-Phenylene di-3-hydroxybenzamide (Reference GW 3-68-108)



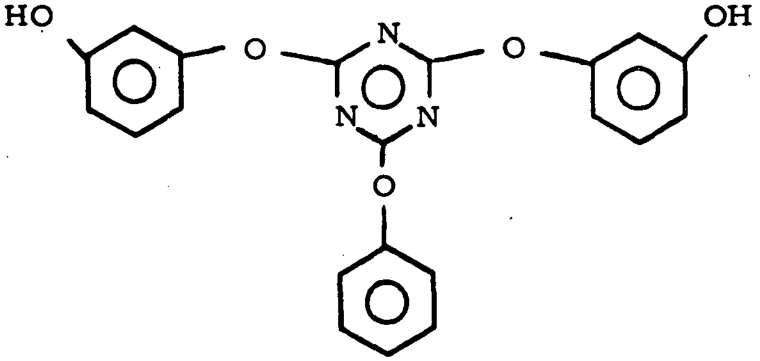
Meta phenylene diamine (10.8 g), $NaHCO_3$ (16.8 g) and 300 ml of water were mixed and heated in a one-liter Morton flask until solution was effected. Heat was removed and 31.3 g of m-hydroxybenzoyl chloride dissolved in about 100 ml of THF was added. The solid product thus obtained was collected, washed with water, and crystallized from a methanol-water mixture. The dried product weighed 22.5 g and melted at 246-249°. Preston and Huffman disclose this compound in a French patent.[8] IR scan Appendix I.

Analysis: Calc. for $C_{20}H_{16}N_2O_4$

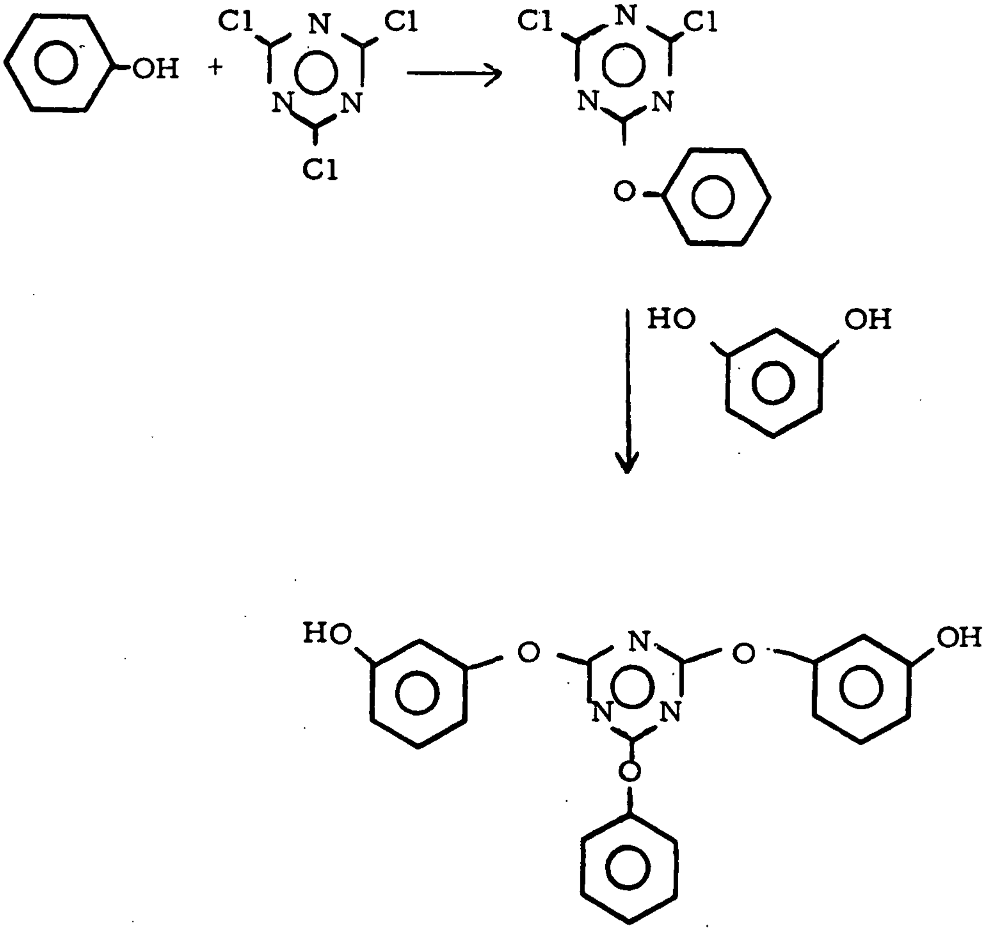
Calc:	C	68.96	Found:	C	64.1
	H	4.63		H	5.5
	N	8.04		N	7.4

11.

2, 6-di(3-hydroxy phenoxy)-4-phenoxy 1, 3, 5 triazene

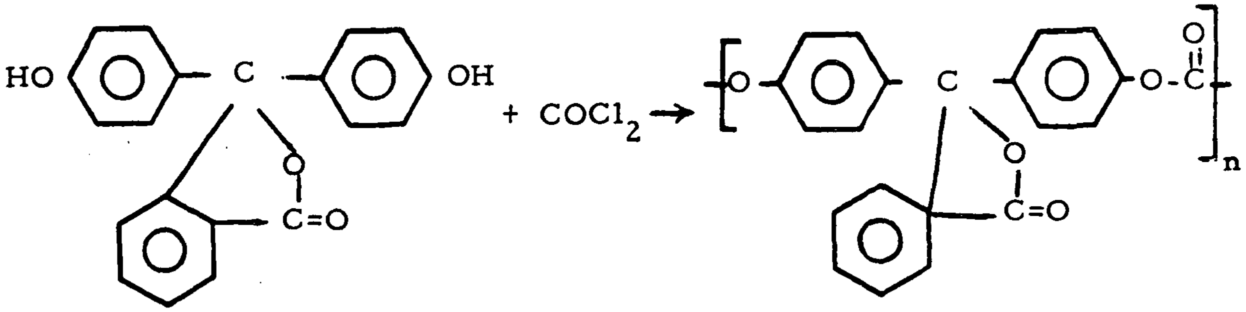


This interesting monomer was prepared in crude form only. Purification was difficult and a detailed study was not possible. The synthesis was a two-step reaction involving reaction of phenol with cyanuric chloride producing the monophenyl ether followed by reaction with resorcinol. The proposed reaction sequence was based upon work of Hirt[9] and Nakamura, et al[9a].



Polymer Preparation

1. Phenolphthalein Polycarbonate (Reference GW 14-69:149)



The reaction was conducted using a 5 liter Morton flask having provision for N_2 or phosgene addition as well as an effluent gas caustic scrubber. Phenolphthalein (95.4 g), tetramethyl ammonium chloride (25 g), 2-1/2 liter methylene chloride and 200 ml of water were all placed in the flask after which sodium hydroxide (40 g in 80 ml of water) was added. A brisk N_2 stream was passed through the stirred solution. Phosgene was then bubbled into the well stirred mixture (N_2 flow was reduced). After about 2 hours the color had faded to a light pink and about 20 ml of 25% caustic was added. This regenerates the color, but continued phosgene flow discharged the color; however, color was regained when caustic was added. This cycling titration, using phosgene and caustic, was repeated eight times, the color being discharged faster on successive cycles until finally no color resulted when caustic was added. Roughly nine hours was required to accomplish this. The emulsion was stirred overnight (no phosgene addition, but slow N_2 flow) and then acetic acid was carefully added (foams) after which the polymer phase was leached with water eight times and then acetone added to precipitate the polymer. The collected polymer was washed with acetone and then hexane, and dried. Dry weight was 81 g. This was redissolved in methylene chloride and washed with dilute caustic, dilute acetic acid, and then water; precipitated using acetone, washed with ethanol, acetone, hexane, and then dried, yielding 49-1/2 g of polymer. $Visc_{(inh)} = 1.28$, T_g 270°.

Several literature reports exist involving this polymer. J. Howe of the Dow Chemical Company first disclosed the polymer[10]. Subsequently Morgan[11] in 1964 and later Russian reports[12] mentioned the phenolphthalein polycarbonate.

Characterization of the polymer included the following:

a) T_g

b) TGA

c) IR

d) Mass Spec

e) Tensile data

f) X-Ray

g) Inherent Viscosity

h) Solubility

a) Glass Transition Temperature (T_g)

The measurement of the T_g was by differential scanning calorimeter (DSC) and also differential thermal analysis (DTA). Interpretation was difficult because of the small inflection point. With some samples it was debatable whether a transition point was detectable. Appendix II gives examples of this data. Measurements were also made on solvent cast film as well as precipitated powder.

b) Thermal Gravimetric Analysis

This determination was made in air and was useful in ascertaining whether the cleanup procedure was adequate. Best samples of the polymer had no weight loss in air upon heating to 400° C. (See Appendix II).

c) Infra-Red Spectra

Spectra was recorded using a thin solvent cast film. (Appendix II)

d) Mass Spectra

The fragmentation pattern was determined using the polymer powder (Appendix II). It should be emphasized that the data presented here was determined from volatile products produced by heating the polymer in a high vacuum.

e) Tensile Data

Preliminary tensile properties were determined using test specimens prepared in the following manner.

1) Dry polymer (finely divided) was mixed with an equal weight of dichloromethane and placed at room temperature in a Carver 2-1/4" compression mold at 2000 pounds overnight.

2) The resulting clear disk was then placed in a 3" x 3" compression mold and, using heat and pressure, was remolded. Depending upon the solvent content, flow occurred prior to 150°F at 5000 pounds ram force (5-3/4" ram).

3) The clear molded square was then placed in a circulating atmosphere and the solvent content allowed to drop to 30%. The sample was then remolded at 200°F and 20, 000 pounds. Further treatment furnished a sample ultimately subjected to 500°F and containing about 10% volatiles. The specimen was light yellow, free of bubbles, but had hazy regions.

4) Tensile test specimens were then punched from the molded square using the ASTM D1708 Microtensile die. The thickness was nominally 1/8 inch. These samples were then vacuum and heat treated until free of volatile matter. Final treatment was at 135°C at 1 mm for several days. Volatile content was followed using TGA (Appendix II).

5) The solvent free samples were then filed in an attempt to remove flaws resulting from the sample cutting.

f) X-Ray

X-Ray examination of the phenolphthalein polymer powder failed to reveal crystallinity. Microscopic examination of a film under polarized light verified the amorphous nature of the polymer.

g) Inherent Viscosity

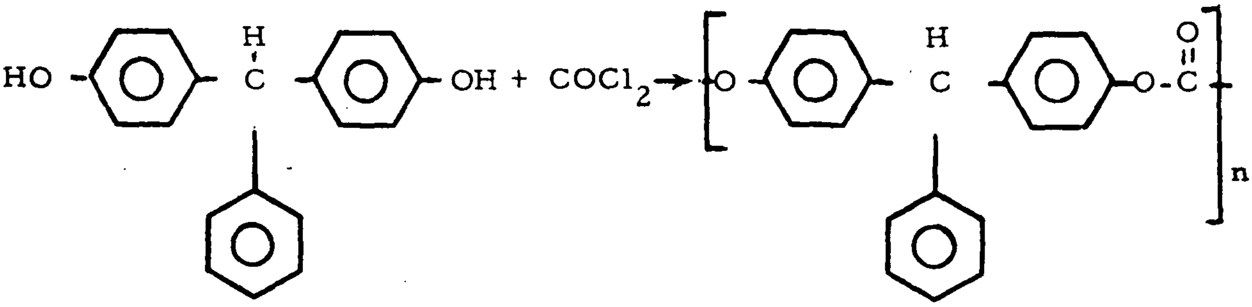
Determined using a 0. 5% dichloromethane solution. Calculated using the formula presented in Sorenson[13].

h) Solubility

The phenolphthalein polycarbonate was soluble in the following solvents.

1. Dichloromethane
2. Chloroform
3. Dimethylformamide
4. Pyridine
5. Sym-tetrachloroethane
6. Dioxane
7. Cyclohexanone
8. 1,2-Dichloroethane
9. N-Methylpyrollidone
10. m-Cresol

2. 4,4'-Dihydroxytriphenyl methane Polycarbonate (Reference GW 14-69:172)



The reaction was conducted using a 5-liter Morton flask. The triphenylmethane derivative (55 g), 2 g tetramethyl ammonium chloride, 2 liters methylene chloride, and 1500 ml water were mixed and 8 g of sodium hydroxide was added. The mixture was stirred vigorously and phosgene passed into the emulsion. The reaction was monitored by periodically sampling the water phase and insuring that it remained basic, (if the pH was lower than 9, caustic was added). At the end of the reaction no starting material was detectable in the basic aqueous phase. The polymer was isolated by precipitation of the entire mass with methanol. Repeated washing with methanol and vacuum drying yielded 43 g.

Visc.$_{(inh)}$ 0.68, T_g 182°, PMT - 220-230°C.

Characterization

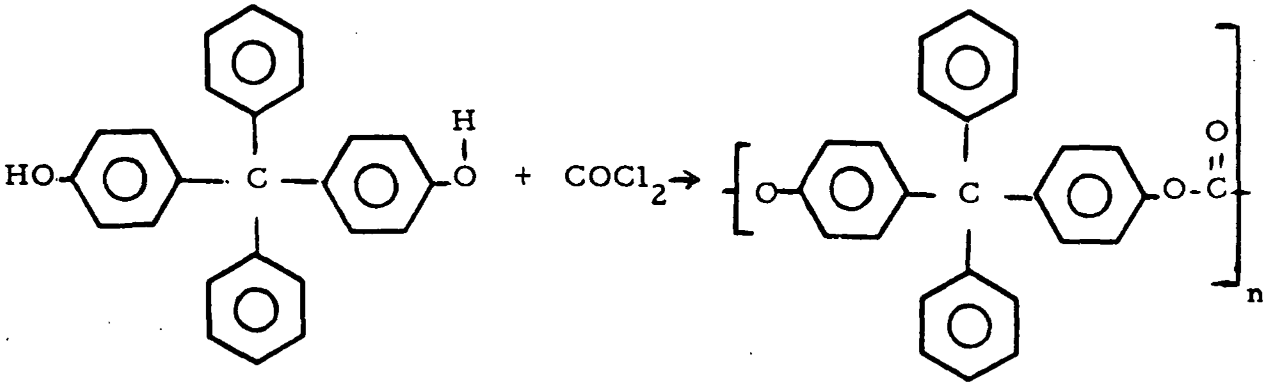
A glass transition temperature of 182°C was determined via DSC (Appendix II). The literature values for this polymer were lower, 120°[14] and 170°. The latter value, a Russian reference[15] was essentially equivalent to the value reported here. Utilizing an empirical relationship T_g/Tm (°K) = 455°/503° = 0.9. This ratio[16] is in the same range as reported ratios for polycarbonates, and, while no more than an approximation does indicate that the low T_g, (120°)is in error.

IR Spectrum - Appendix II

TGA - Appendix II

PMT (Polymer Melt Temperature) - 220-230°

3. 4,4'-Dihydroxytetraphenyl methane Polycarbonate (Reference 14-69:178)



The reaction was accomplished using a 2-liter Morton flask. The tetraphenylmethane derivative (58.7 g), tetramethyl ammonium chloride (6 g), 800 ml of methylene chloride and 500 ml water were efficiently mixed and 40 g of a 50% aqueous caustic solution was added. A nitrogen atmosphere was maintained by bubbling N_2 through the emulsion. Phosgene was then bubbled into the emulsion. The reaction was monitored by periodically sampling the water phase and insuring the pH was over 9 (if not, caustic was added). After five days of intermittently adding phosgene, the reaction appeared complete. The emulsion was acidified with acetic acid and the methylene chloride phase separated and washed with water several times, and then added to isopropyl alcohol. The precipitated polymer was collected and washed successively with isopropyl alcohol and hexane. The dried polymer weighed 27 g.

Viscosity$_{(inh)}$ 0.64 T_g 213° - PMT 260°

Characterization

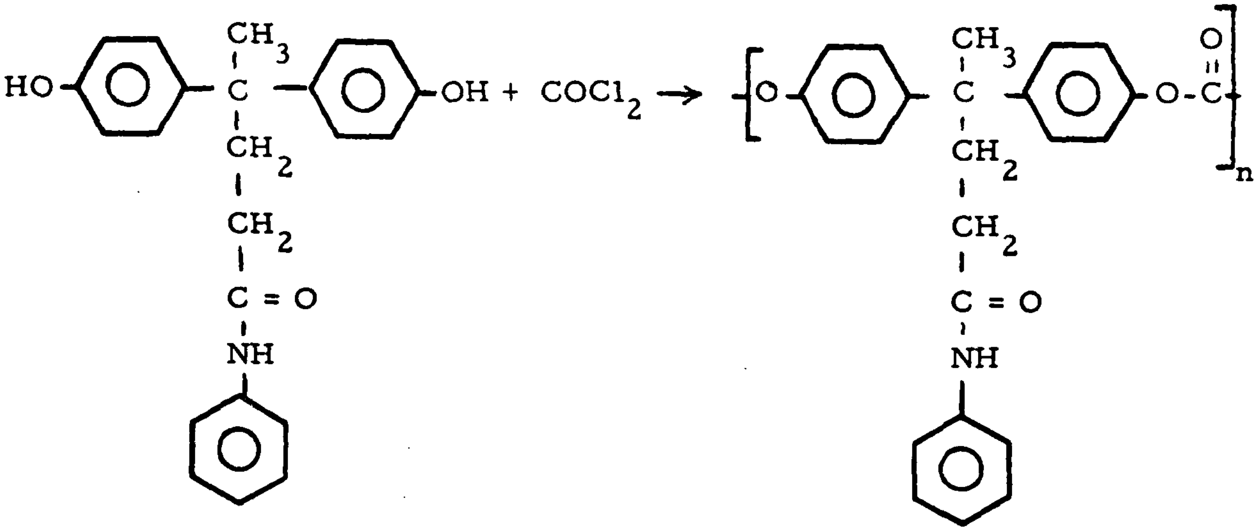
T_g. A 213° (Appendix II) glass transition temperature was considerably above a reported literature value[17]. Utilizing the empirical relationship involving the ratio T_g/Tm (°K) = 486/533 = 0.91, a factor was obtained that was consistent with the ratio determined for the triphenyl homologue.

IR Spectrum - Appendix II

TGA - Appendix II

PMT - 260°C

4. Diphenolic Anilide Polycarbonate (Reference GW 14-69:173)



A 500 ml Morton flask was filled with 3.61 g diphenolic acid anilide, 0.5 g tetramethyl ammonium chloride, 150 ml methylene chloride, 100 ml water, and finally, 1 g of caustic. Phosgene was added to the stirred emulsion. The reaction was monitored by sampling the water phase to insure it remained basic and that monomer was still present. At the later stages of the reaction, the polymer precipitated from solution. This solid was collected and washed with methanol using an air-driven Waring blender. The dried polymer weighed 2 g and was insoluble in methylene chloride

$\text{Viscosity}_{(inh)}$	0.59 (DMF)
T_g	164°
PMT	190°

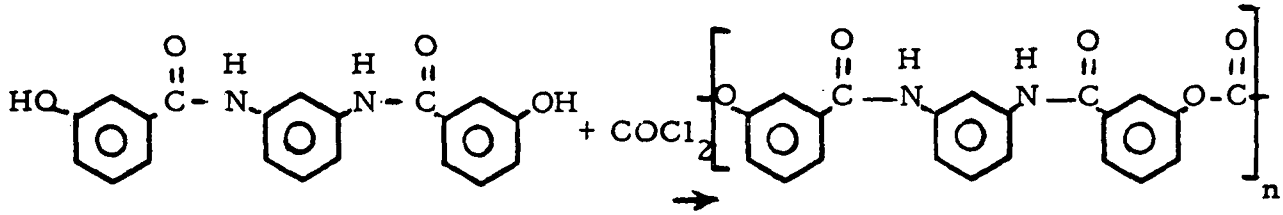
This polymer was not characterized. Polymers of this type were disclosed in the patent literature[18], but this polymer was not described.

IR Spectrum - Appendix II

T_g - Appendix II

TGA - Appendix II

5. m-Phenylene Di-3-hydroxybenzamide Polycarbonate (Reference GW 14-69:173)



A one-liter Morton flask was used for this reaction. Provision was made for addition of N_2 and phosgene gas and any effluent gases were passed through a caustic scrubber. The bisphenol (6.8 g), 1 g tetraethyl ammonium chloride monohydrate, 200 ml of methylene chloride, and 200 ml of water with 4 g of aqueous 5% caustic were mixed; then phosgene was bubbled through the emulsion. After a short time, a solid appeared and after one hour, a test of the aqueous phase for monomer was negative. The solid was collected and washed with acetone and then dried. Yield - 6.2 g; insoluble in methylene chloride and pyridine. The polymer was not fully characterized. Polymers of this type were disclosed [8], but not described in patent literature.

$\text{Viscosity}_{(\text{inh})}$	0.22 (DMF)
T_g	260° (crystalline melting point)

Decomposes at 310°

IR Spectrum - Appendix II

T_g - Appendix II

PILOT PLANT PREPARATION

Equipment

The polymerization runs were made in a 20-gallon reactor in the Pilot Plant area. The sequence of operations was shown as a block diagram earlier. The reactor was a standard glass-lined Pfaudler equipped with a three-blade turbine agitator and a single thermowell baffle. The agitator was driven by a variable speed air motor (10 to 150 rpm). The heat exchange jacket was maintained with cooling water to hold the reactor temperature at about 25 °C.

The reactor was loaded through the standard 4-inch flange opening which was then closed with a thick glass window. A Teflon sparge tube extending below the liquid level on the reactor was used for adding phosgene gas and N_2 for purging. A side valve above the sparger was installed to allow the addition of CH_2Cl_2 as required to prevent plugging. Phosgene gas was supplied from a steel cylinder chained to a stand which was balanced on a scale. Flow was controlled by a needle valve through copper tubing to a rotameter and then through polyethylene tubing to the sparger. The N_2 purge gas was vented into a NaOH scrub bottle to remove any unreacted $COCl_2$ and then into an exhaust duct to the main building scrub column. Caustic solution (10 wt. % NaOH) was pumped into the reactor with a Masterflex pump from a storage jug calibrated by volume.

Description of Run

Prior to each run the reactor was cleaned by heating and flushing the interior with CH_2Cl_2 and then drained. The vessel was purged with N_2 for 0.5 hours and then loaded in the following manner:

1. Poured in 4.0 gal. of CH_2Cl_2.
2. Started agitator at ~10 rpm and decreased the N_2 purge stream.
3. Poured in 3.0 lb. of dry phenolphthalein (1360 g, 4.28 moles) and allowed to disperse in the CH_2Cl_2.
4. Poured in 4.0 gal. of distilled water.
5. Added as catalyst 68 g. of tetramethyl ammonium chloride in 0.2 l of water.
6. Added as anti-oxidant 10 g. of $Na_2S_2O_4 \cdot 2H_2O$.

The loading port was closed with a glass lid and fastened tightly.

The caustic solution was prepared by diluting 4.0 lbs. of 50% NaOH with 16 lbs. of distilled water and mixed in the feed jug. The pump was operated to purge and fill the lines with caustic and then connected to the feed inlet at the top of the reactor. Three liters of the 2.8 N NaOH were pumped into the reactor in 5 minutes. The charge of NaOH was approximately equivalent to the phenolphthalein and the mixture was stirred 15 minutes to allow for dissolution of the monomer in the aqueous phase and dissipation of the heat of neutralization.

The phosgene cylinder was weighed and then supported on a scale (100 lb. capacity) in an upright position to deliver gaseous $COCl_2$. Connections were completed, the scale was balanced, the gross reading recorded, and flow of $COCl_2$ was started to the reactor. All fittings were inspected for leaks with test paper sensitive to trace amounts of phosgene. No $COCl_2$ was detected from the cylinder, the feed lines, or from the vent lines entering or leaving the NaOH scrub trap. The flow was adjusted to 70 on the rotameter equivalent to a rate of about 6.5 oz/hr. or 3 g $COCl_2$/min. The reaction mixture was stirred vigorously, the temperature maintained at ~ 23 °C, and $COCl_2$ vapor added through the sparge tube until the red color faded to white as viewed through the glass port. The flow of $COCl_2$ was stopped but the N_2 purge and stirring were maintained. This initial cycle of phosgenation required 2 hours and the scale reading indicated that 13 oz. of $COCl_2$ had been added.

A 1 liter quantity of the 2.8 N NaOH was pumped in and the reaction mixture became deep red. Phosgene flow was resumed at 60 on the rotameter and maintained until the decline in NaOH concentration resulted in fading of the red color. This second cycle required 32 minutes and 3 oz. of $COCl_2$.

Alternate additions of NaOH and $COCl_2$ were continued for a total of 9 cycles. As the cycles proceeded, the amounts of NaOH and the flow rates of $COCl_2$ were reduced. In the later stages, less red color developed when NaOH was added but some phenolphthalein monomer remained at the end. At intervals, 1 liter batches of CH_2Cl_2 were added through the sparge tube to prevent plugging and to dilute the CH_2Cl_2 phase in the reactor. The viscosity of the mixture increased as the molecular weight of the polymer increased. A total of 8.7 liters of additional CH_2Cl_2 was used.

After the final cycle the phosgene cylinder was removed and weighed. The net consumption of $COCl_2$ was 29 oz. (8.34 moles) or 195% of the phenolphthalein on a mole basis. The total NaOH used was 9.5 liters of 2.8 N (26.6 eq.) or 310% of the monomer on an equivalent basis.

The total reaction time to the end of the final $COCl_2$ cycle was 10 hours. The reaction mixture was stirred with no additions for 12 hours to allow for increase in polymer molecular weight and was then acidified with 1.5 liters of 6N HCl to a pH of 3-4. The acidified mixture was stirred for 1 hour and then drained from the reactor into polyethylene storage jugs.

The emulsified reaction mixture was allowed to separate and the aqueous phase containing some emulsion was discarded. The CH_2Cl_2 phase (24. liters) was viscous, very cloudy, and nearly colorless. The polymer was precipitated from the CH_2Cl_2 by the addition of acetone, the cloudy liquid phase was discarded, the solids were re-dissolved in CH_2Cl_2, and the solution was washed twice with water. The purified polymer solution was filtered twice through Celite to remove any insoluble impurities and entrained water. The clarified solution was precipitated by slowly adding to an equal volume of hexane with vigorous agitation. The solids were soaked in hexane, filtered, and dried under vacuum at 80°C for 24 hours.

The quantities of reactants used in the seven polymerization runs are shown in Table I. Details of the reaction conditions and the results obtained are given in Table II.

TABLE I

QUANTITIES USED

(Polycarbonate Scale UP)

Run No.	Phenolphthalein		CH_2Cl_2, liter		Water, liter	A g	B g	NaOH		$COCl_2$		Vol. of 6 N HCl liter
	g	moles	Initial	Additional				Volume of 2.8 N liter	Eq/ eq of Phth	g	mole/ mole of Phth	
1	1360	4.28	15.2	14.0	15.2	68.	5.	20.5	6.69	1660	3.90	1.5
2			15.2	10.2	14.5	68.	4.	17.0	5.55	1300	3.10	1.2
3			15.2	5.6	15.2	68.	5.	10.3	3.37	880	2.08	1.2
4			14.9	15.2	15.2	68.	6.	10.3	3.37	910	2.15	1.2
5			15.2	5.3	15.2	68.	8.	10.7	3.50	1020	2.41	1.0
6			15.8	8.7	15.2	68.	10.	9.5	3.10	824	1.95	1.5
7			14.9	2.3	15.2	68.	8.	8.0	2.61	880	2.08	1.9

A Catalyst, tetramethyl ammonium chloride

B Antioxidant, $Na_2S_2O_4 \cdot 2H_2O$

TABLE II

REACTION CONDITIONS AND RESULTS

(Polycarbonate Scale UP)

Run No.	Number of Cycles	Reaction time, hr.		Temp., °C	Phase Separation	Color	Estimated Yield		Inherent Viscosity dl/g ***
		$COCl_2$ Addition	After $COCl_2$				Dry Polymer, g	% of Theory**	
1	*	10.	15.	23±2	Poor	Fair	1385.	94.	1.3
2	*	9.	16.	23±2	Poor	Fair-good	1160.	79.	0.7
3	9	9.5	15.	23±2	Fair	Fair-good	1100.	75.	0.6
4	10	13.5	12.	23±2	Poor	Fair	1300.	89.	1.2
5	8	11.5	13.	23±2	Good	Good	1350.	92.	1.1
6	9	10.5	15.	23±2	Good	Good	1270.	87	1.0
7	7	10.	15.	23±2	Poor	Fair	1300.	89	1.2

* After the first cycle, NaOH + $COCl_2$ added simultaneously.

** Theoretical yield = 1360 x 344/318 = 1470 g.

*** In methylene chloride at 25 °C. 0.5% solution.

Results and Comments

The object of this program was to prepare a quantity of high molecular weight phenolphthalein polycarbonate resin sufficient for fabrication of test panels. Process conditions were used which were found to be suitable and no concerted effort was applied to attain higher efficiency. Preliminary tests on a small scale indicated that tetramethyl ammonium chloride used at 5 wt. % based on phenolphthalein was effective as catalyst and that quantity was used in all the pilot runs.

This system is sensitive to degradative oxidation in the initial stages when phenolphthalein and NaOH concentrations are very high. The anti-oxidant, sodium dithionite, was somewhat effective in preventing color formation and the amount used was increased to 8-10 g in the later runs. Purging of air from the system with N_2 was also effective.

Rather large excesses of NaOH and $COCl_2$ were used especially in the first two runs. Repeated additions of NaOH and $COCl_2$ were applied in attempts to connect all of the monomer and build the molecular weight. However, it can be seen from the results of Runs 6 and 7 that good polymer was obtained with approximately 2 moles of $COCl_2$ per mole of phenolphthalein. The inherent viscosity of the products was measured in CH_2Cl_2 at 25 °C and was typically 1.0 to 1.2 dl/g. at 0.5% concentration.

Estimates of total yield were made by determining the weight of product per liter on a small scale and calculating from the total volume for the run. During the processing, some of the lower molecular weight polymer was excluded due to solubility in acetone and the yields shown are for the fractionated material. In Runs 1 and 2, the yields were lower due to greater rejection of soluble lower fractions. The theoretical yield was based on the molecular weight of a repeating unit which is equal to phenolphthalein + CO - 2H or 344 g/mole.

The phase separation characteristics of the reaction mixtures were variable. In some cases separation was very poor and the thick emulsion required two days for complete isolation of the CH_2Cl_2 phase. In others, separation was complete in 15 minutes. Generally, when poor separation occurred for the reaction mixture, it was also a problem during aqueous washing of the polymer solution.

PANEL FABRICATION

General Considerations

The fabrication of sheets or plastic glazing is well documented in the literature and it is not intended to discuss these methods in any detail; however, the basic features of each process and key property requirements that could relate to PPR fabrications are mentioned below.

1. Compression molding. This is the direct molding of polymer in a heated mold. The method is simple and direct. To succeed the polymer has to respond to heat, pressure and be melt stable. Melt viscosity has to be such that entrapped bubbles can be caused to flow out of the polymer.

2. Extrusion. Basically nothing more than the calendering of molten polymer into flat sheets. Prime requirement for fabrication is that the melt stable polymer have a melt viscosity of machine acceptability.

3. Polymerization in place. The method requires a liquid monomer or prepolymer to polymerize with no volatile release. The approach requires exotherm control and any volume change observed in going to the solid state has to be negligible or else residual strains and stresses have to be relievable.

4. Solution Casting. This method involves the build-up of a thick film to sheet thickness. In the simplest case it approximates a surface coating. This fabrication method can be adapted to virtually any soluble polymer. Major difficulties encountered are insuring that complete solvent removal can be accomplished and that residual stresses developed during solvent removal can be relieved.

5. Fusion of a Plastisol. This method avoids the requirement of melt stability by utilizing an intimate mixture of polymer and plasticizer. Application of heat and pressure by use of heated rolls initiate solvent action ultimately producing a clear sheet. The basic requirements for this method to be successful are that plasticizer polymer interaction be satisfactory and the system be stable at the processing temperatures.

6. Powder Forming or Forging. This basically is the compression molding of a heated preformed billet or blank. The blank is heated to a temperature in the region of the Tg or Tm and then quickly molded. Prime requirement is that the polymer can be preformed into a dense billet and be stable to the preheating treatment.

7. Celluloid Sheet Manufacture.[19] This involves the following operations:

    a. Cellulose nitrate is mixed with a carrier solvent (ethanol) and a permanent plasticizer (camphor).

    b. The uniformly mixed system is pressed to shape.

    c. Controlled removal of volatile components is then accomplished.

    d. The final product contains camphor as permanent plasticizer and residual tracer of ethanol (~2%).

The key feature to note is that the camphor-alcohol combination yields with cellulose nitrate, a material having thermal properties (Tg and Tm) dependent upon the relative amounts present. These thermal properties, as solvent removal occurs change, ultimately approaching the properties displayed by the non-volatile camphor-cellulose nitrate combination.

The fabrication method chosed for PPR was governed by the inability to satisfactorily melt flow the polymer. Consideration of the various fabrication methods and their key requirements with respect to PPR resulted in the following table.

PPR FABRICATION

	Key Property Requirements				
Fabrication Method	Melt Stable	Stability at Tg Region	Solvent Solubility	Liquid Monomers	Adaptable to PPR
Compression Molding	✓				No (A melt stable polymer is required)
Extrusion	✓				No (A melt stable polymer is required)
Polymerization in Place				✓	No (A liquid monomer pre-polymer is required)
Solution Casting			✓		Yes
Plastisol Fusion			✓		No (Contract goals do not permit inert additives)
Powder Forming		✓			Yes
Celluloid Type Production			✓		Yes

Examination of this table reveals that three possible approaches can be selected. The contract goals requiring fabrication of unadulterated polymer panels eliminated a fourth approach, plastisol fusion, since a permanent plasticizer forms the basis of this method. An expediency factor eliminated powder forming leaving two methods, namely, solution casting and celluloid type production. These methods are basically similar in that volatile materials are removed. This removal of volatile material (really a plasticizer) results in a polymer system that undergoes a Tg change as the volatiles are removed. The Tg slowly approaches that of the base polymer, with the result that the polymer chain mobility becomes less and less; hence continued removal of fugitive plasticizer becomes less and less favored. To appreciate the magnitude of this the following data has been presented regarding a "favored" system, celluloid[19].

Sheet Thickness (Inches)	Time Required to approach 2% volatile content - 120°F circulate air.
0.01	3 days
0.05	7 days
0.1	14 days
0.25	24 days
1.0	56 days

This favored system contains about 25% by wt. camphor which results in necessary chain mobility and with such a mobility the removal of the more volatile alcohol is permitted.

With regard to a "less favored" system such as PPR, an excellent case can be made for claiming that the final traces of volatile material are effectively locked into the polymer and will never diffuse to the surface. Naturally temperature is a factor in such a system; however, prolonged heating in a vacuum at high temperature results in undesirable color formation. This contract, on the basis of the preliminary test specimens, set a volatile content specification of no greater than 2% wt. loss on heating to 300°C. Thin specimens could easily be treated to attain this volatile level, but the larger panels were difficult to reduce below 3-4% and this value is more realistic.

Procedure

The general procedure for fabrication involved the following steps:

1. Polymer powder is swollen with acetone.
2. When volatiles are about 40% by weight, the plasticized mass is molded at temperatures up to 230°C and 1,000 psi.
3. The volatile content is then allowed to drop to about 15-20% by weight.
4. The specimen is replasticized by immersion in dichloromethane.

5. Remold at 200°C and 1,000 psi.

6. Place in a vacuum oven and slowly heat the panel to 150°C until of acceptable volatile content. This will be from one to two months.

Equipment Used

Two compression molds were used. The trial specimens were prepared using a 3" x 3" x 3/4" cavity mold of tool steel. The larger test panels were prepared using a 9" x 11" x 2" cavity mold with the plug and the bottom plate made of carburized steel. Cauls used were Mylar sheets for lower temperature work and for higher temperatures Apollo brand Mirror Finish Chromed Ferrotype plates were used. The hydraulic press was a Pasadena Hydraulic 50 ton capacity with a temperature capability of 600°F.

Characterization of Bulk Polymers

A total of ten panels were prepared using the above procedure or variations of it. The best optical quality panels were obtained using the above steps. The polymer used to prepare these panels was from seven pilot plant production runs. The bulk polymer had the following characteristics.

Production Number	Inherent Soln. Visc.
1	1.12
2	0.64
3	0.64
4	1.14
5	0.93
6	0.93
7	1.15

Characterization of the bulk polymer was to include the following seven items:

1. Inherent solution viscosity (0.5% in CH_2Cl_2)
2. TGA in air and nitrogen to 800°C with no more than a 1% wt. loss observed upon heating to 390°C. The 390°C weight loss data was determined on all seven plant production runs. Data in Figures 26-32. Behavior to over 700°C was observed in air and nitrogen on two runs, run No. 4, nitrogen, and run No. 5, air. Complete oxidation by 700°C was observed using an air atmosphere and a 54% wt. loss by 850°C was observed with nitrogen. Generally with a 15° a minute heating rate no difference in onset of decomposition temperature was observed using air or nitrogen atmosphere, indicating the initial mode of decomposition was thermal with oxidative effects not observable. A detailed study would be required to clarify the decomposition modes.
3. Infra-red and ultra-violet spectra. Infra-red data is presented in the monomer section of the experimental work. The ultra-violet spectrum is presented in Figure 33.
4. The Tg (via DTA) is recorded for one polymer in Figure 34.
5. Color (Gardner scale) of a 5% CH_2Cl_2 solution. The color of the dichloromethane solution was two or less in all cases. Generally the color was less than one.
6. Solubilities. The solubility in common solvents was found to be good, providing the solubility parameter was in excess of 9.3. The parameter for the polymer is 10.4.

SUITABLE SOLVENTS

Weak H Bonding Solvents	Moderate H Bonding Solvents	
CH_2Cl_2 -- 9.7	Dimethyl phthalate	10.7
$CHCl_3$ -- 9.3	Dioxane	9.9
1,2 dichloroethane -- 9.8	Cyclohexanone	9.9
1,1,2,2 tetra chloroethane -- 10.4		

7. Elemental Analysis and Residue or ignition

a. Elemental analysis on typical polymer calculated for

$C_{21}H_{12}O_5$	C	73.25%
	H	3.51%
found	C	73.2%
	H	3.4%

b. The residue left upon igniting a 2 g. sample was less than 1 mg. or 1 part in 2000.

c. Trace metals

Na - < 7 ppm
Fe - <14 ppm

No specifications regarding molecular weight were required. A rough correlation involving GPC data based upon polystyrene standards was observed. These values are only a guide since polystyrene would be expected to have different retention times than PPR.

Inherent Viscosity of PPR	Number Average Mol. Wt.
0.64	42,000
0.93	145,000
1.14	155,000

PANEL FABRICATION

(See Table III)

Panel No. 1 -- from Plant Run No. 2 solution viscosity (inherent) 0.64.

Results

This panel was rejected. Extensive degradation and fracture of the panel occurred. The failure was indicated by determining a solution viscosity (inh) of only 0.2 from a fragment of the panel.

TABLE III

CONTRACT NAS2-6388

TEST PANELS

Panel Number	Comments	Viscosity Specification a)		Thermal Behavior to 300°C (wt. loss)
		Before	After Fabrication	
1	Reject, Fragments	0.64	0.2	Not checked
2	Reject[b], completely opaque, but intact	1.12	0.52	2%
3	Reject[b], due to crazing	0.64	0.42	3%
4	Poor quality, no craze	1.14	0.31	2%
5	Poor quality, some crazing	0.93	0.54	3%
6	Poor quality, no craze	0.93	0.98	2%
7	Fair quality, no craze	1.15	1.04	2%
8	Fair quality, no craze	0.93	0.70	2%
9	Fair quality, no craze	0.93	0.85	3.4%
10	Good quality, no craze	1.15	0.52	3%

a) Inherent Viscosity (0.5% in CH_2Cl_2).

b) On account of flaws or degradation panel not suited to physical strength measurements, but suitable for determination of thermal behavior.

Fabrication

There was mixed with 400 g. of PPR polymer an equal weight of dichloromethane. Mixing was difficult and some areas were not mixed uniformly. The mass was allowed to stand overnight in a closed container during which time evaporation occurred furnishing a relatively uniform looking polymer mass. There was removed 10% of the mass (80 g.) of material for fabrication of the trial sample (discussed later). The remainder was placed in a 9" x 11" compression mold (with Mylar cauls) and the plastic mass was shaped into a flat sheet. The shaped mass was removed from the mold and supported upon a stainless steel expanded metal grate and nitrogen was circulated over a 24 hour period resulting in some weight loss. When volatiles were as 30% level the shrunken mass was repressed without cauls in the 9" x 11" mold at 150°C and 750 psi. Upon cooling, the sheet was trimmed of flashing, (and solvent content reduced to 15-20% level) and then remolded without cauls at 175-210°C with pressure up to 1,000 psi. The cooled sample was brittle and had regions of pronounced dark spots. The contact of the steel with the polymer at elevated temperatures resulted in an iron catalyzed decomposition of the thermally unstable dichloromethane. The viscosity (inh) of the broken sheet was only 0.2. Extensive degradation had occurred.

The trial specimen was similarly treated excepting that polished chromed ferrotype cauls were used. The non-iron surface prevented any catalyzed decomposition from occurring and the 3" x 3" trial specimen upon checking for viscosity drop was found to be 0.58 or roughly a 10% reduction. Devolatilization was accomplished by the following process:

a. Circulating 50°C oven 1 week.

b. Circulating 100°C oven 3 days.

c. Vacuum oven, R.T. 3 days.

d. Heated vacuum oven 3 days at 50°C, 3 days 100°C, 5 weeks 130°C. Volatile content after this time was less than 2% total wt. loss upon TGA examination to 300°C. The viscosity of polymer cut from the sheet was 0.58.

Panel No. 2 -- from Plant Run No. 1, solution viscosity (inh) 1.12.

Results

This panel was a reject because of numerous craze regions as well as probable hydrolysis or degradation of the polymer. The panel was opaque, but completely intact. Degradation was indicated by the fact that polymer sampled from the panel yielded a solution inherent viscosity of only 0.52.

Fabrication

The panel was prepared at the same time as the previous panel excepting that complete mixing of the 400 g. of polymer with distilled dichloromethane was accomplished by grinding the polymer (dry) in a Waring blender followed by sieving through a 24 mesh screen. This sieving operation insured that particle size was uniform. Controlled evaporation of the dichloromethane proceded until volatile content was 33% of the total. The soft mass was then molded at 135°C at a pressure of 250 psi. The cooled sheet was then reduced in solvent content over an 18 hour interval by use of a nitrogen stream. When the solvent level was at the 20% level the sheet was opaque due to either too rapid removal of the dichloromethane (chilling action coupled with condensation) or to the screening operation introducing trace contaminates resulting in degradation. Remolding at increasingly higher temperatures did not improve the opacity. Final molding was at 200°C at 1,000 psi. Devolatilization was accomplished by heating at 50°C for one week followed by a vacuum treatment at R.T. for two weeks and then increasing the temperature of the sample to 50° (3 days), 100°C (1 week), and finally 135°C for 2 months. The inherent viscosity of polymer cut from the panel was 0.52 (down from 1.12). The wt. loss upon heating to 300° in air by TGA analysis was less than 2%.

No trial sample was prepared.

Panel No. 3 -- from combined Plant Runs 2 and 3, viscosity (inh) 0.64.

Results

This panel had craze regions in it and, while clear, was a reject. Polymer degradation was not as extensive as evidenced by a viscosity (inherent) of 0.42 being obtained on the fabricated sample.

Fabrication

A similar procedure as for Panels 1 and 2 was followed except that the 400 g. of polymer after mixing with dry distilled dichloromethane was carefully protected from moisture while controlled evaporation was allowed to proceed. Ten percent of the mass was removed to permit preparation of a trial specimen. At the 40% volatile level the mass was molded at 75 °C and then the crude panel was carefully conditioned in a nitrogen stream until volatile content was at the 20% level. Remolding at 150°C followed by a later molding at the 10% level (220°C) furnished a panel that upon devolatilization developed craze regions near the surfaces. Conditioning to remove the volatiles was the same as with Panel No. 2 except that the final vacuum oven treatment was at 140°C. The finished panel after two months in a vacuum oven at this temperature underwent no further weight loss. Examination revealed that a 3% wt. loss was observable upon TGA analysis to 300°C. Polymer sampled from the sheet was readily soluble in dichloromethane and a solution viscosity of 0.42 (inh) was observed.

The trial sample was treated similarly except that heat up times were appreciably shorter and devolatization required one month. The trial sample when volatile free (less than 2% wt. loss by 300°C) had a viscosity of 0.52.

Panel No. 4 -- from Plant Run No. 4, viscosity (inh) 1.14.

Results

The panel had very little crazing, but it was optically of poor quality. Degradation occurred, for the completed panel had a viscosity of 0.31.

Fabrication

The procedure used for Panel 3 was followed. When the volatile content had been reduced to 12-16%, a major crack, bubbles, and distortions developed. The sheet was immersed in dichloromethane for 15 minutes, after which a molding at 200°C and 1,000 psi was performed (lot of flashing). The repaired sheet was then devolatilized, first at 50°C, then in a heated vacuum oven. Some craze developed during this time. After devolatilization at 140°C for 2 months in a vacuum oven, a panel was obtained that underwent less than a 2% wt. loss upon TGA examination to 300°C. Polymer sampled from the panel yielded a solution viscosity (inh) of 0.31.

The 3 x 3 trial sample after devolatilization did not undergo extensive degradation.. Polymer cut from the specimen had a viscosity of 0.97.

Panel No. 5 -- from Plant Run No. 5, viscosity (inh) 0.93.

Results

The completed panel had some craze regions as well as dark spots even though titanium cauls were used in an effort to eliminate decomposition of dichloromethane. The dichloromethane is thermally unstable and long heating times result in some solvent decomposition which releases HCl and ultimately degrades the polymer. The completed panel furnished polymer having a solution viscosity of 0.54.

Fabrication

The procedure followed for Panel No. 5 fabrication was the same as for Panel No. 4 except that the solvated polymer, when at the 40% volatiles level, was molded using titanium cauls. These cauls were used exclusively for Panel No. 5 preparation to insure that no iron contamination was introduced during fabrication. The color of the panel was noticeably improved by the use of a titanium contacting surface. Treatment otherwise was the same as for Panel No. 4. Following devolatilization, a TGA examination resulted in less than a 3% wt. loss on heating to 300°C. The solution viscosity (inherent) of polymer removed from the panel was 0.54. No trial specimen was prepared.

Panel No. 6 -- from Plant Run No. 5, viscosity (inherent 0.93).

Results

The panel was prepared using an acetone-dichloromethane mixture for plasticizing liquid. The acetone is a swelling solvent and it was reasoned that it, in conjunction with some dichloromethane, would permit a more rapid devolatilization of plasticizer as well as sharply reduce the processing cycles and resulting polymer degradation. This, in fact, happened, for the sample, following devolatilization, furnished a polymer solution viscosity (inherent) of 0.98. This value was about 10% higher than the starting polymer and presumably simply reflects experimental error.

Fabrication

A 400 g. quantity of dried polymer was added to a 1600 g. -80 g. mixture of acetone-dichloromethane. Following complete mixing, the polymer mass consistency went to a rubbery dough with excess liquid being present. This was decanted and the solvent content allowed to approach 40% level. This mass was sampled for a trial specimen (10% removed), and the plasticized mass, now a grainy translucent material was molded successively at 100°C (250 psi) 150°C (300-500 psi) and 220°C (1,000 psi). The completed panel was then devolatilized over a 2 1/2 month period ultimately at 140%, 140°C (vac). A TGA analysis to 300°C resulted in a 2% wt. loss, and the solution viscosity (inherent) of polymer from the panel was 0.98.

A trial specimen was prepared which followed a similar treatment and resulted in a less than 2% wt. loss upon heating to 300°C.

Panel No. 7 -- from Plant Run No. 7, viscosity 0.93.

Results

This panel was prepared like Panel No. 6 except that flawed regions necessitated a dunking in dichloromethane to resolvate the panel surface. This treatment simply involved placing the panel in dichloromethane for a short time (about 15 min.) followed by remolding at 200°F (1,000 psi). The completed, devolatilized panel had a 2% wt. loss on heating to 300°C, and the polymer from the panel had a solution viscosity (inherent) of 1.04.

Fabrication

The procedure for Panel No. 6 was followed except that bubbles developed in the panel and it was necessary to correct these defects by resolvating the panel surfaces by short immersion in dichloromethane followed by remolding at 200°C (1,000 psi). Devolatilization then proceeded as with Panel No. 6. The completed panel had a 2% wt. loss upon heating to 300°C and polymer from the panel had a solution viscosity (inherent) of 1.04.

A trial 3" x 3" specimen was prepared except that flaws did not develop in it and an immersion in dichloromethane was not needed.

Panel No. 8 -- from Plant Run No. 6, viscosity (inherent) 0.93.

Results

This panel was prepared using production polymer solution. The polymer was used directly from the reaction kettle and not isolated as a dry polymer. The panel prepared by direct evaporation of reaction solvent was of poor quality possibly because of hydrolysis or degradation. The panel was opaque; as was the trial specimen. The large panel had a viscosity of 0.70.

Fabrication

Filtered reaction solution from the purification stage, which was then carefully evaporated by initially distilling solvent from the solution. Starting quantity was 3.85 liter of about 5% polymer content and this was concentrated first by distillation and then by "nitrogen" stream to 550 g. of polymer mass. A portion (10%) was removed for trial panel preparation and the main mass was then pressed into a sheet using the mold. The formed sheet was further devolatilized and remolded at 150°C and 500 psi pressure. Further devolatilization introduced bubbles which were removed by resolvating the surface with dichloromethane and subsequent molding at 150°C and finally 210°C. The sheet was light yellow, but opaque. At the completion of devolatilization the solvent content was 2% upon heating to 300°C and the panel yielded polymer with a solution viscosity (inherent) of 0.70.

The 3 x 3 trial specimen also was opaque.

Panel No. 9 -- from Plant Run No. 5, viscosity (inherent) 1.15.

Results

This panel was prepared by simply treating the polymer with acetone and solvating. The excess solvent was then allowed to evaporate and the residue, containing about 20-30% of acetone was pressure molded at 150°C - 200°C. Crazing was observed and resolvating with dichloromethane was necessary to achieve a flaw free panel. The devolatilized panel had 3.4% volatile matter and polymer from the panel had a solution viscosity of 0.85.

Fabrication

The panel was prepared by adding 400 g. of dry polymer to 1,600 g. of dry acetone. After standing overnight the polymer mass was of doughy consistency and considerable excess acetone was present. The excess solvent was removed and 10% is removed for a trial specimen. The polymer mass was then formed into a flat sheet.

This was then allowed to evaporate to approximately 30-40% solvent content. The sheet turned to a light yellowish translucent panel and this was then remolded at 120°C (500 psi). Further solvent removal introduced some bubbles which were removed by resolvating the surface with dichloromethane. The final sheet was molded at 230°C at 1,000 psi. The volatiles were removed by a vacuum heated oven treatment over a 2 month period. Volatile content at the final stage had been lowered to 3.4% wt. loss upon heating to 300°C. The solution viscosity (inherent) of polymer sampled from the panel was found to be 0.85.

A trial specimen, 3" x 3", was prepared, but it was not necessary to resolvate the surface with dichloromethane.

Panel No. 10 -- from Plant Run No. 7, viscosity (inherent) 1.15.

Results

The panel was prepared in the same manner as Panel No. 9 except that a longer resolvation treatment was necessary. The completed panel had a 3% wt. loss on heating to 300°C and an inherent viscosity of 0.52.

Fabrication

The panel was prepared in the same manner as Panel No. 9 except that a longer immersion in dichloromethane was necessary to remove defects. The devolatilized panel underwent a 3.4% wt. loss upon TGA examination at 300° and the polymer from the panel had a solution viscosity of 0.52.

The trial specimen was very similar to No. 9 trial specimen.

Panel Quality Estimation

The control of panel quality was difficult. Original contract specifications included optical tests to measure the following:

1. ASTM D 1003-61 Haze and luminous transmittance.
2. ASTM D 1740-70 Transparency.
3. ASTM D -925 Yellowness index.

The tests were not run because of the variability in quality among the panels. The variance was due to the following factors:

A. Instability of dichloromethane at elevated temperatures.

B. Introduction of foreign matter.

C. Surface moisture being molded into the panel (causing moisture streaks).

D. Unequal solvent release causing dirtiness, stresses and bubbles of various types.

These four factors limited panel quality. The physical properties of the panels generally correlated with molecular weight (reflected by the inherent solution viscosity). Contract specifications did not include any provision for physical testing; however, a small amount of data was gathered by use of cuttings from the panels. Panel size for the contract was 8" x 10" x 1/8". Actual fabrication size was 9" x 11" and following completion of panel devolatilization the panels were then cut to contract size yielding roughly 1/2" wide cuttings. These were examined as follows:

Viscosity of Panel Polymer	Panel Number	Impact Notched Izod ft. lbs/" (Number of Samples)	Tensile Yield Stress	Elastic Modulus psi	Flex Modulus
0.70	8	1.47 0.91 (2)	6.77%	412,000	22,000
0.52	10	0.72 (3) 0.85, 0.85	9.25%	403,000	-----
0.31	4	0.50 0.54 (2)	---	---	-----

Thermal Gravimetric Analysis (15°/min., air). The behavior of the polymer to weight loss on heating to 300°C was the means for quality control and all ten panels were monitored in this manner. (Figures 35-43) The 2% observable weight loss was attained for 5 panels using a two months solvent removal treatment. The removal of volatile matter was difficult and four of the panels, due to time considerations, were delivered with 3-3.4% volatile content.

Thermal analysis of panel No. 4 with regard to isothermal aging was as follows:

Temperature °C	3 Hour Isothermal Wt. Loss (in air)
250°C	3.3% weight loss
300°	3.6%
325°	5.8%
350°	16.2%

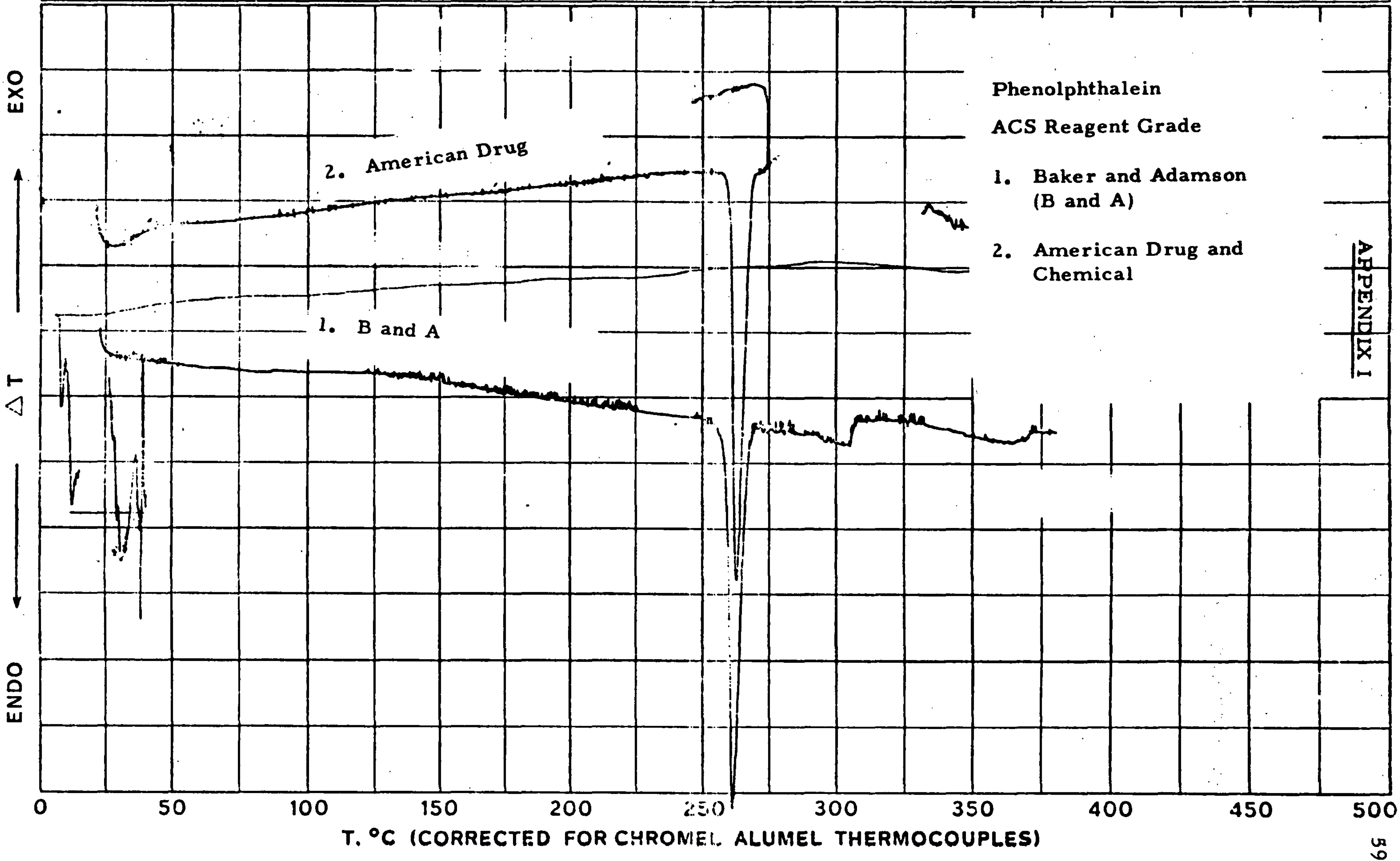
The use of a fugitive plasticizer technique can produce acceptable quality panels; however, it is doubtful that such an approach could succeed in terms of practical production quantities. Excessive time is required to reduce volatile content to a low level (<2%). Assuming that molding of neat polymer is not immediately possible, raising the volatile content to 5% would greatly simplify production procedures and time. Further work is recommended in two areas:

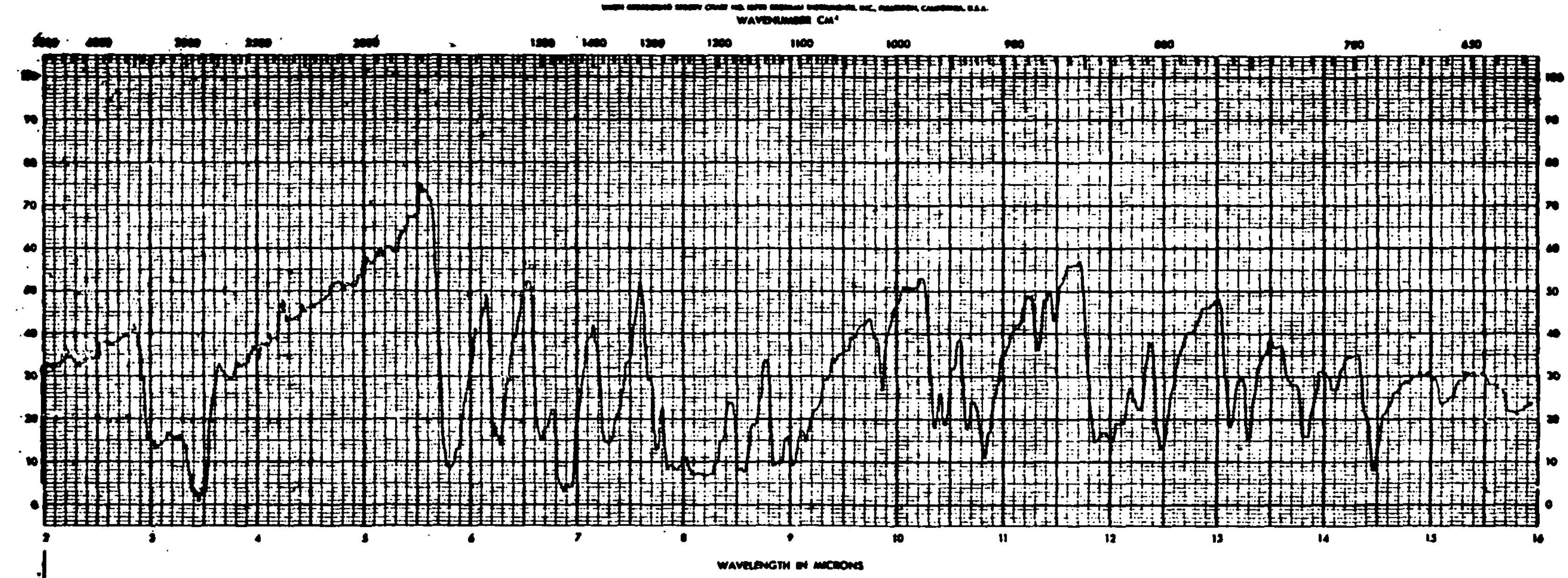
1. Optimization of Fugitive Plasticizer Procedures.
    a. Synthesis and screening program to find or develop a permanent plasticizer that would permit retnetion of most of the polymer properties (some compromise in properties vs. plasticizer content might have to be made).
2. Improvement in Polymer Process and Purification and Stabilization Techniques to permit direct molding of unmodified polymer. This is a practical goal.

APPENDIX

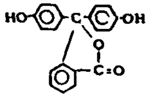
APPENDIX I

SAMPLE: Appendix I Figure 1 Phenolphthalein	SIZE	ATM.	RUN NO.
	REF.	T ΔT	DATE
	PROGRAM MODE	SCALE SETTING 50 °C/in.	OPERATOR
ORIGIN:	RATE °C/min, START °C		



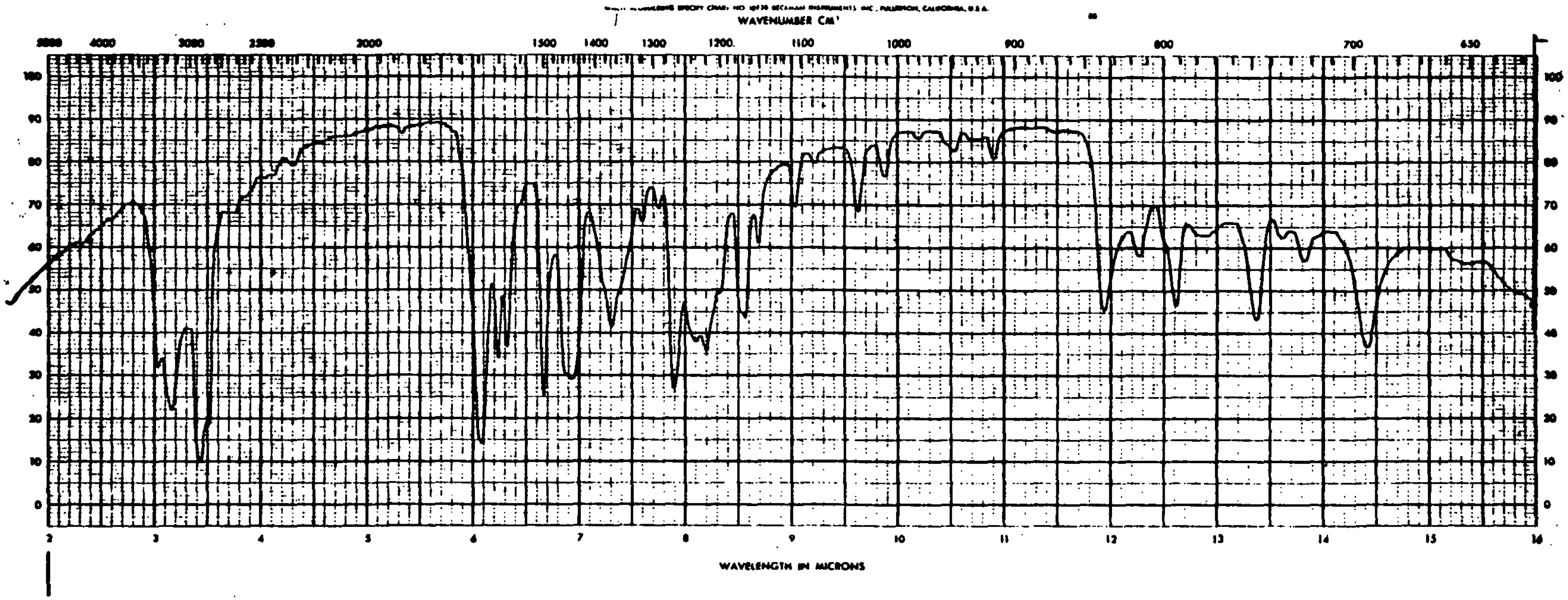


Appendix I
Figure 2
Phenolphthalein
(Band A)
Nujol Mull

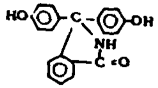


CONCENTRATION ______
PHASE ______
COMMENTS ______
______
______
ANALYST ______

Beckman
INFRARED
SPECTROPHOTOMETER

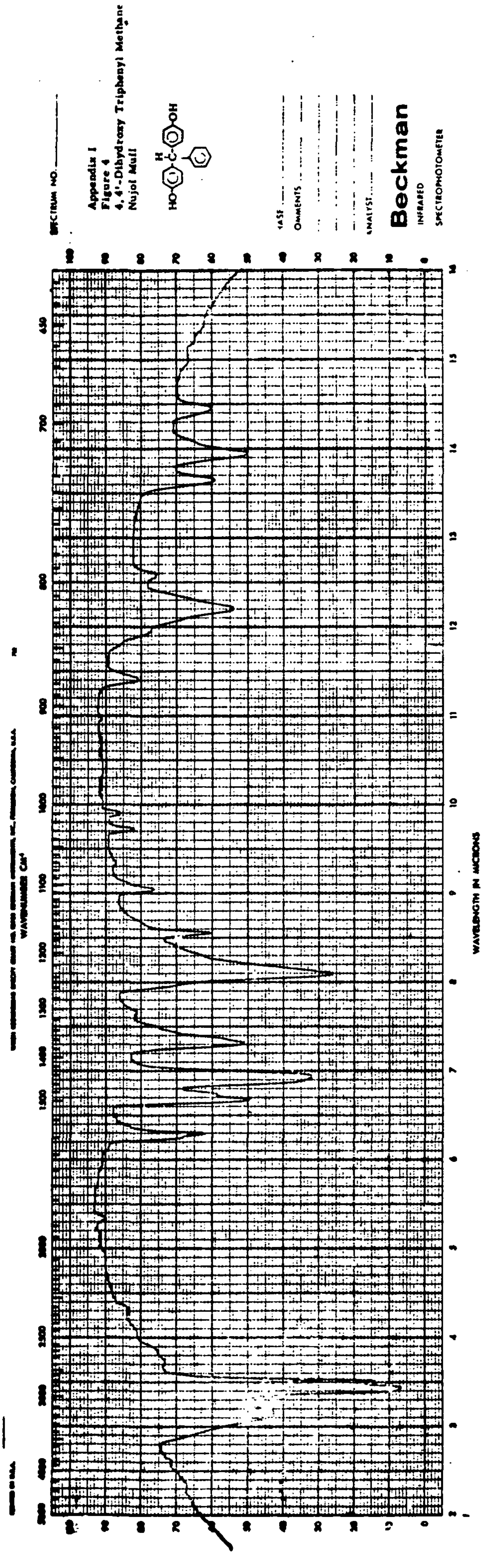


Appendix I
Figure 3
Phenolphthalimidine
Nujol Mull

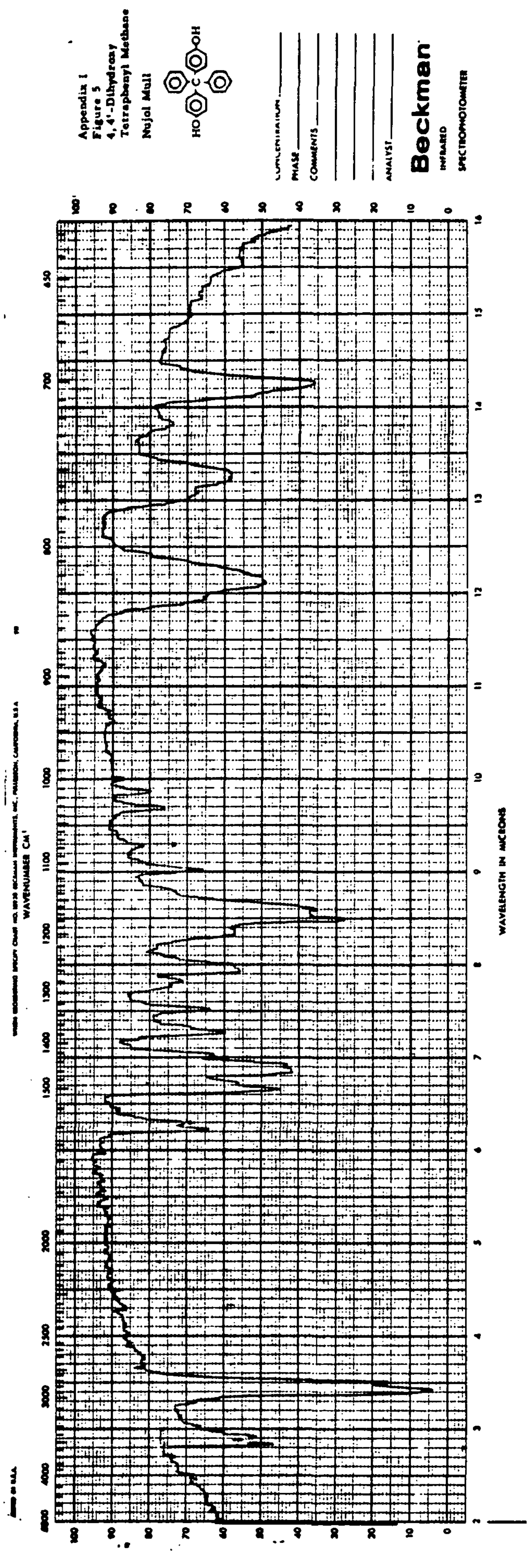


CONCENTRATION ______
PHASE ______
COMMENTS ______
______
______
ANALYST ______

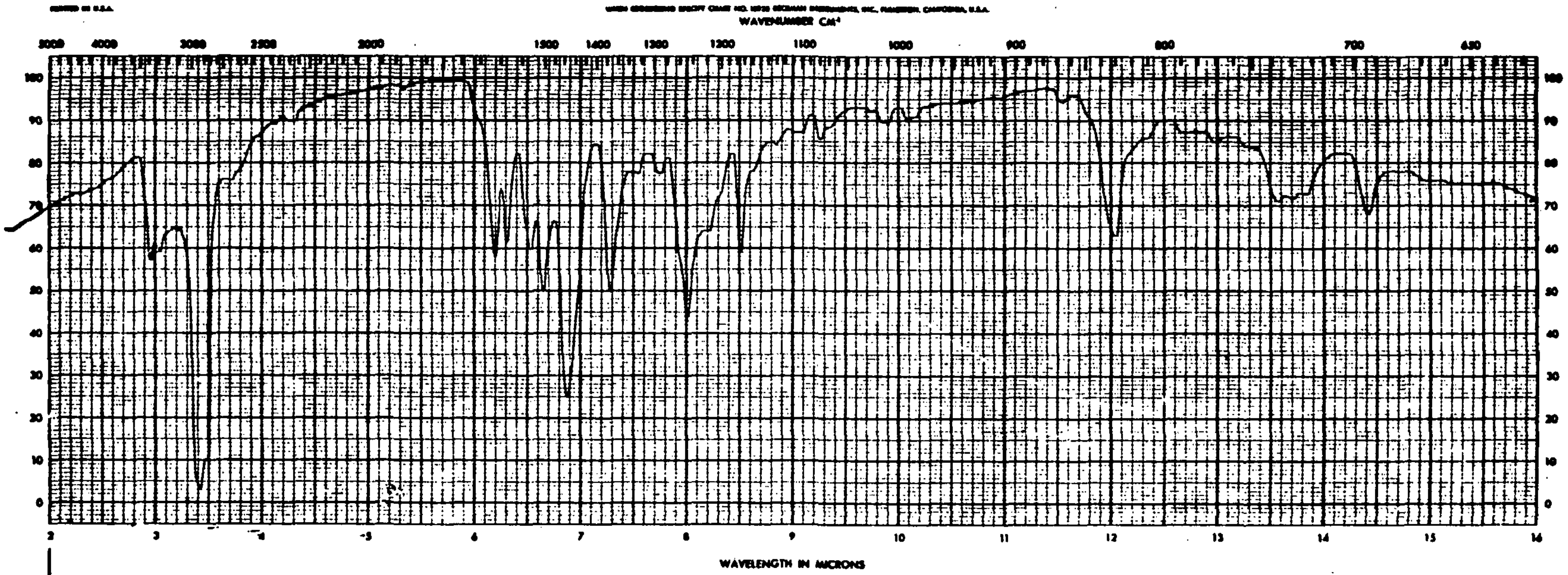
Beckman
INFRARED
SPECTROPHOTOMETER



Appendix I
Figure 4
4,4'-Dihydroxy Triphenyl Methane
Nujol Mull

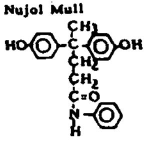


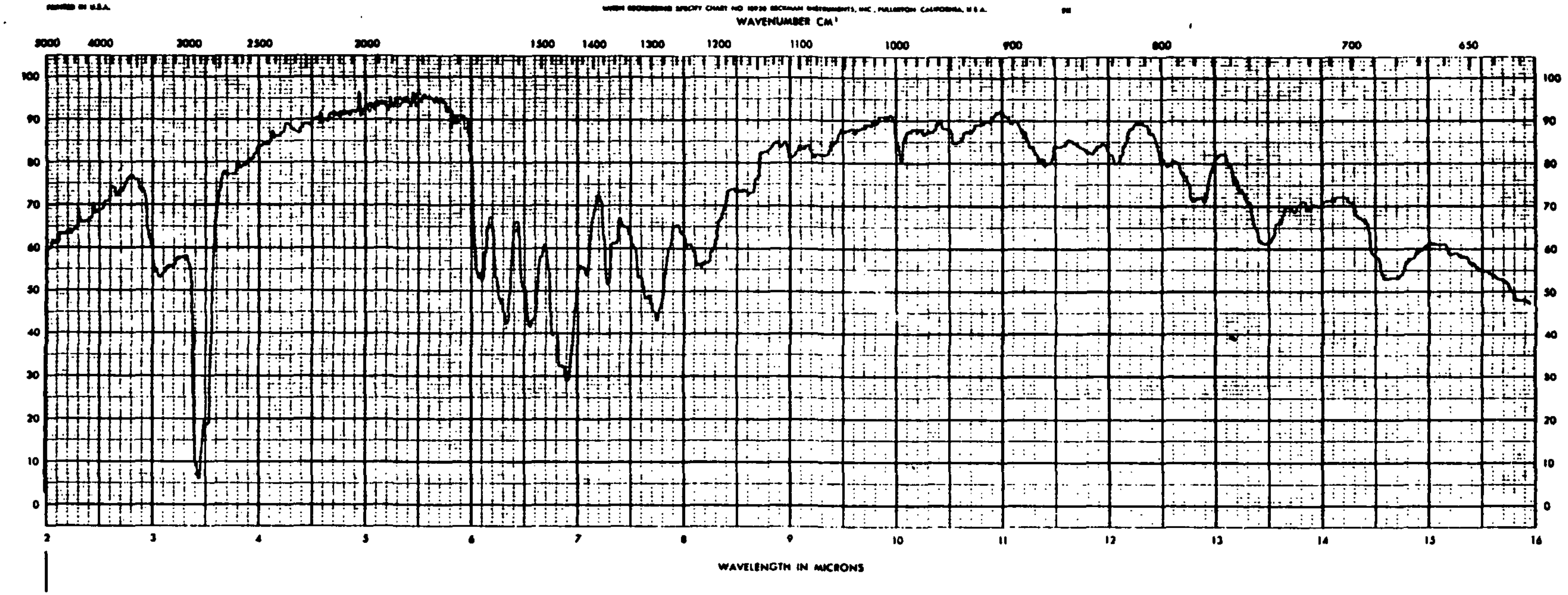
Appendix I
Figure 5
4,4'-Dihydroxy
Tetraphenyl Methane
Nujol Mull



Appendix I
Figure 6
4, 4'Bis(4-hydroxyphenyl)-N-phenylpentanamide

Nujol Mull

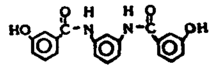


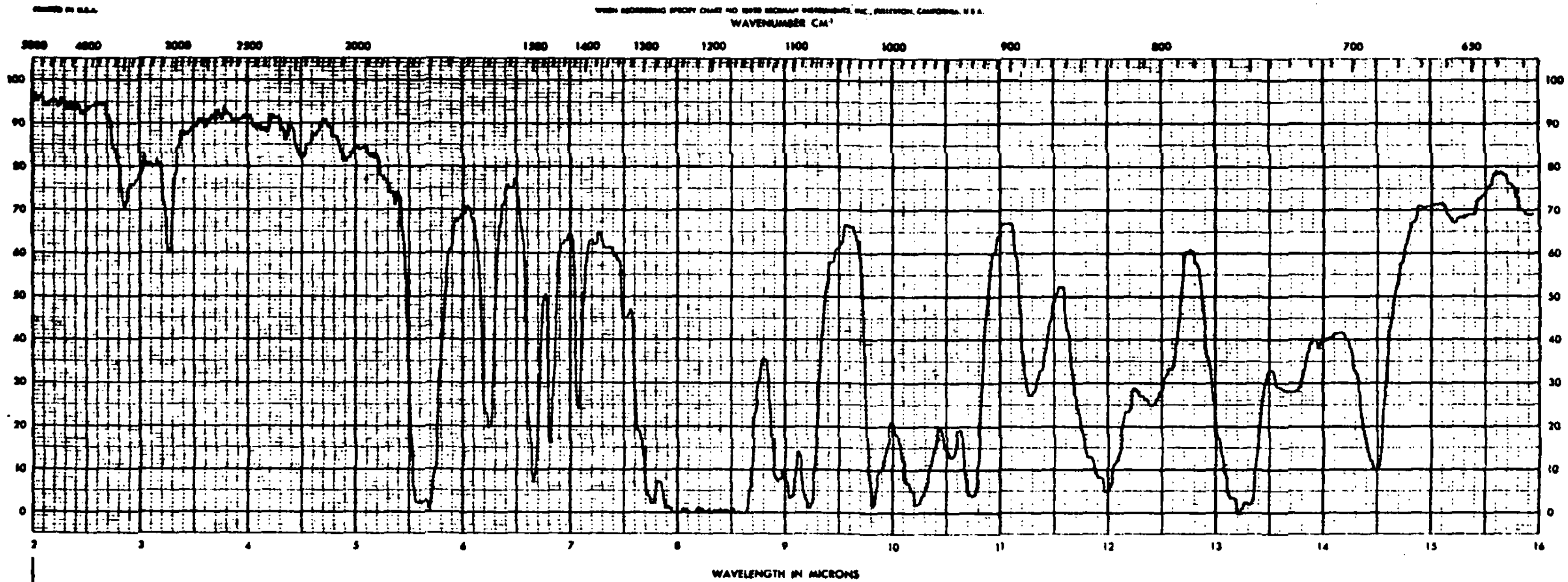


SPECTRUM NO.

Appendix I
Figure 7
N, N'-m-phenylene di-(3-hydroxy benzamide)

Nujol Mull



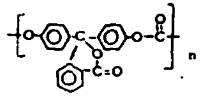


SPECTRUM NO. ____

Appendix II

Figure 8

Phenolphthalein Polycarbonate Thin Film

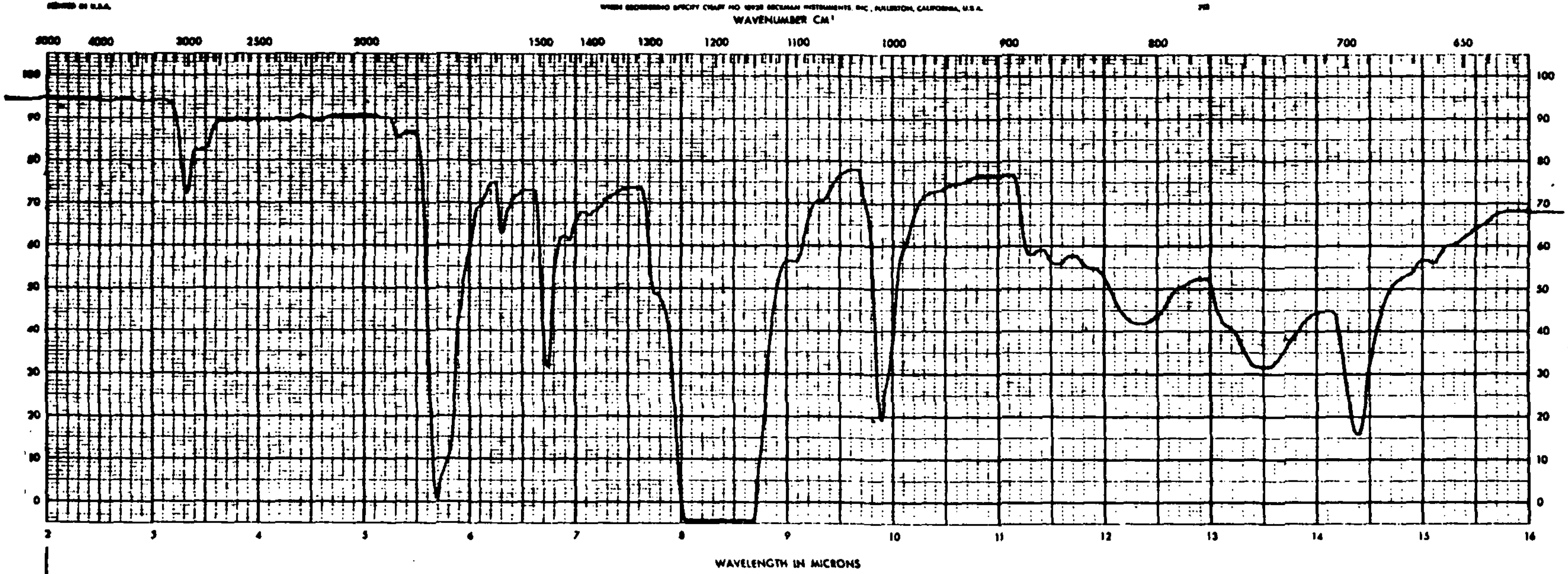


PHASE ____

COMMENTS ____

ANALYST ____

Beckman
INFRARED
SPECTROPHOTOMETER

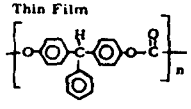


SPECTRUM NO. ____
DATE ____

Appendix II

Figure 9

4,4'-Dihydroxy Triphenyl Methane Polycarbonate Thin Film



COMMENTS ____

ANALYST ____

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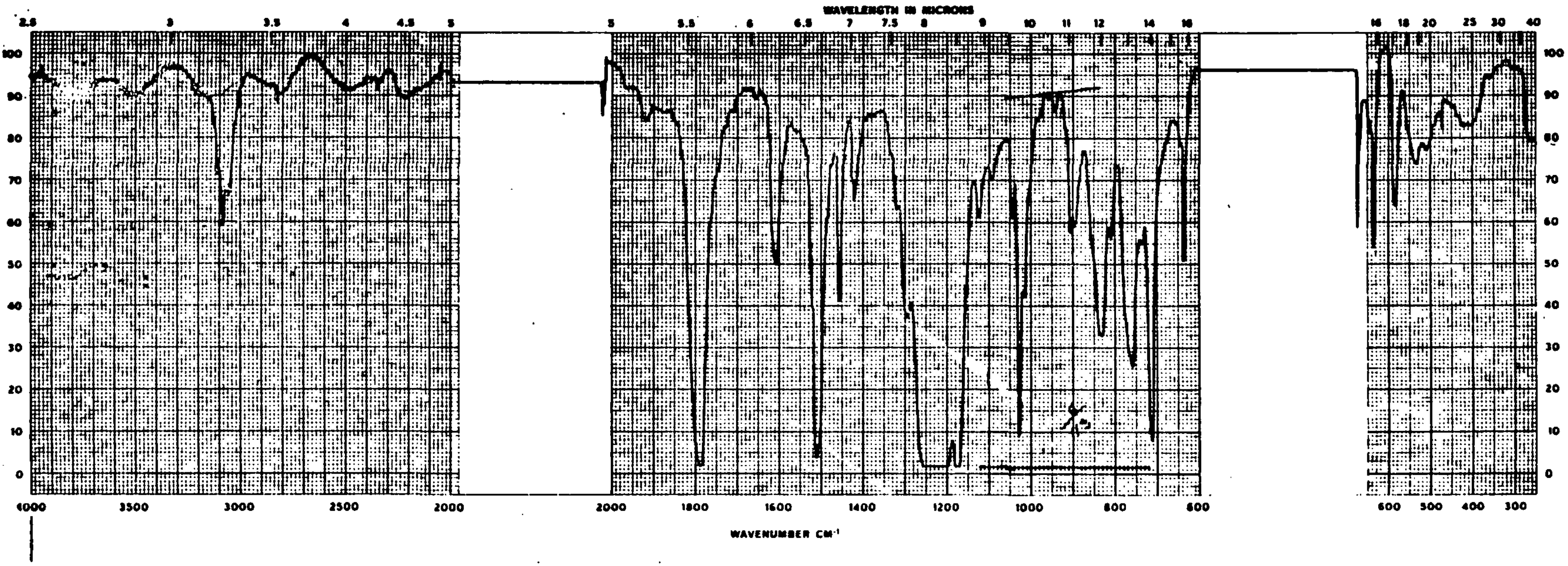
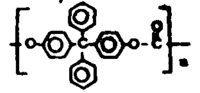
INFRARED
SPECTROPHOTOMETER



Appendix II

Figure 10

4,4'-Dihydroxy Tetraphenyl Methane Polycarbonate
Thin Film



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PHASE

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ANALYST__________

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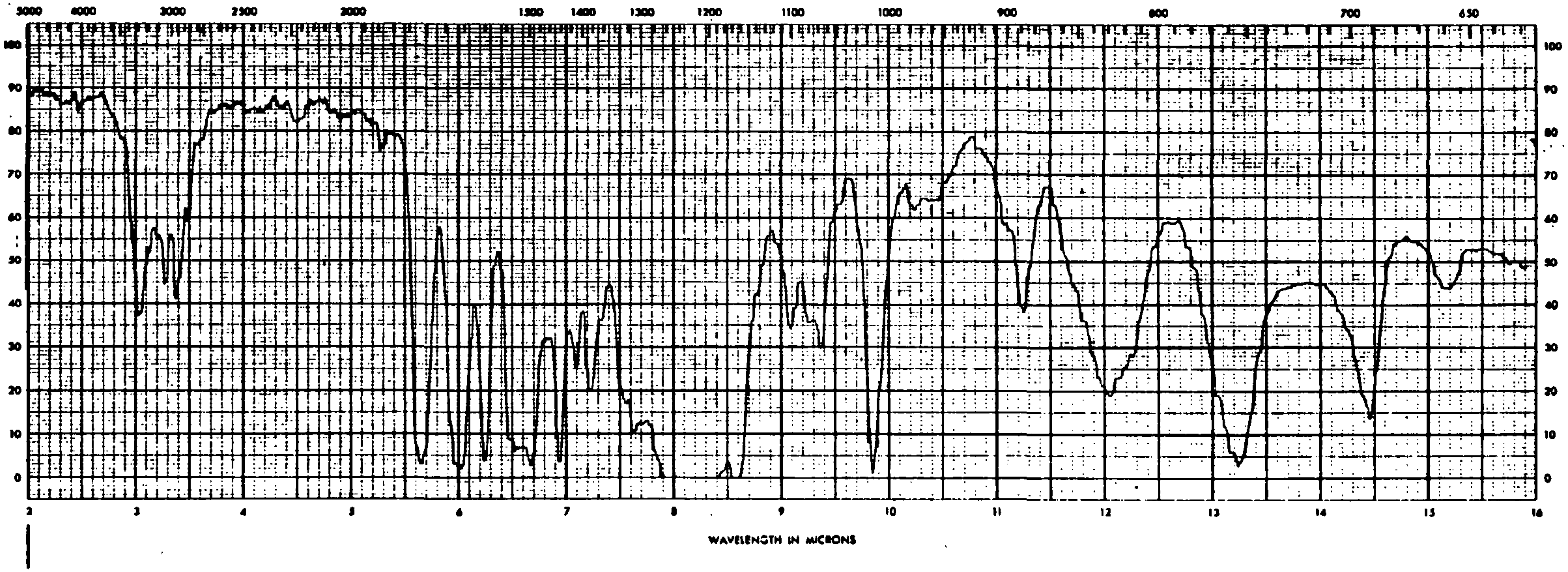
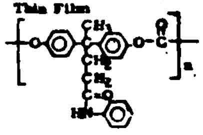


SPECTRUM NO.__________

Appendix II

Figure 11

4,4-Bis(4-hydroxyphenyl)-N-phenylpentanamide polycarbonate
Thin Film



PHASE__________

COMMENTS__________

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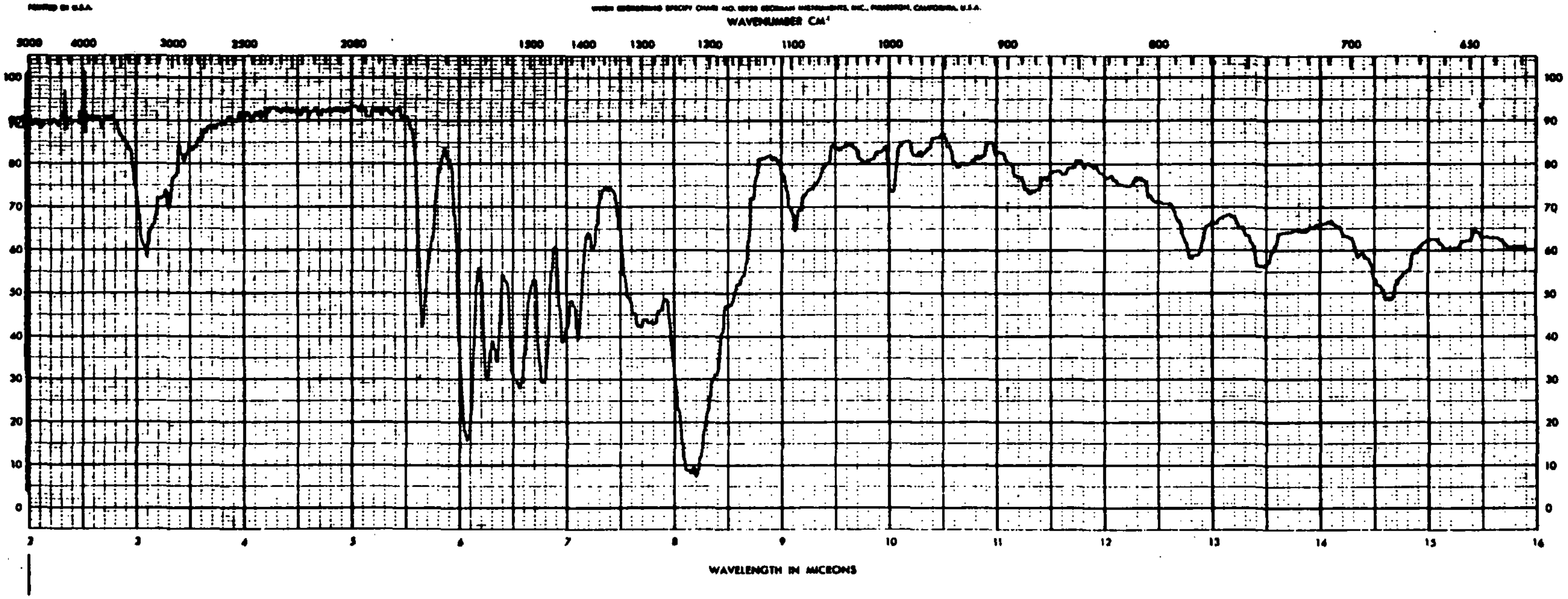
ANALYST__________

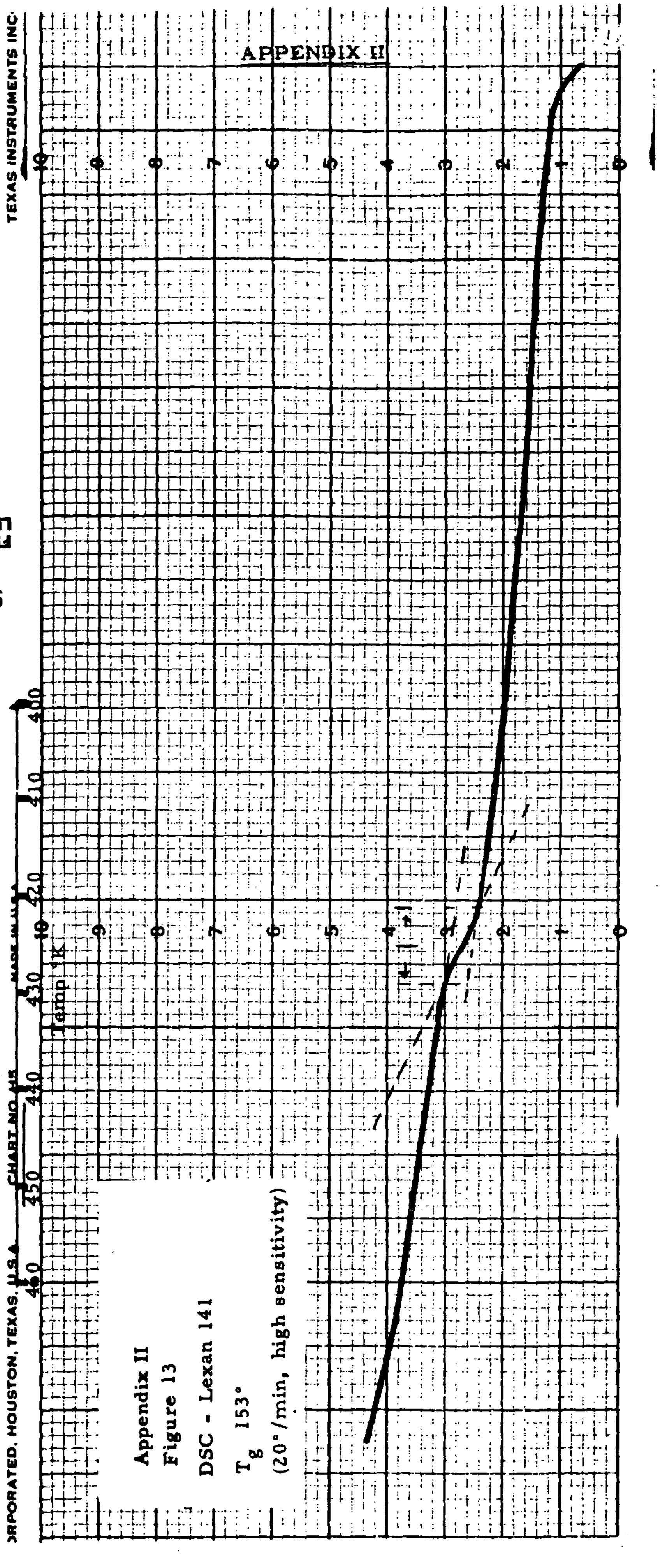
Beckman
INFRARED
SPECTROPHOTOMETER



Appendix II

Figure 18

N,N'-m-phenylene di-(3-hydroxy benzamide) polycarbonate
Thin Film



Appendix II
Figure 13
DSC - Lexan 141
T_g 153°
(20°/min, high sensitivity)

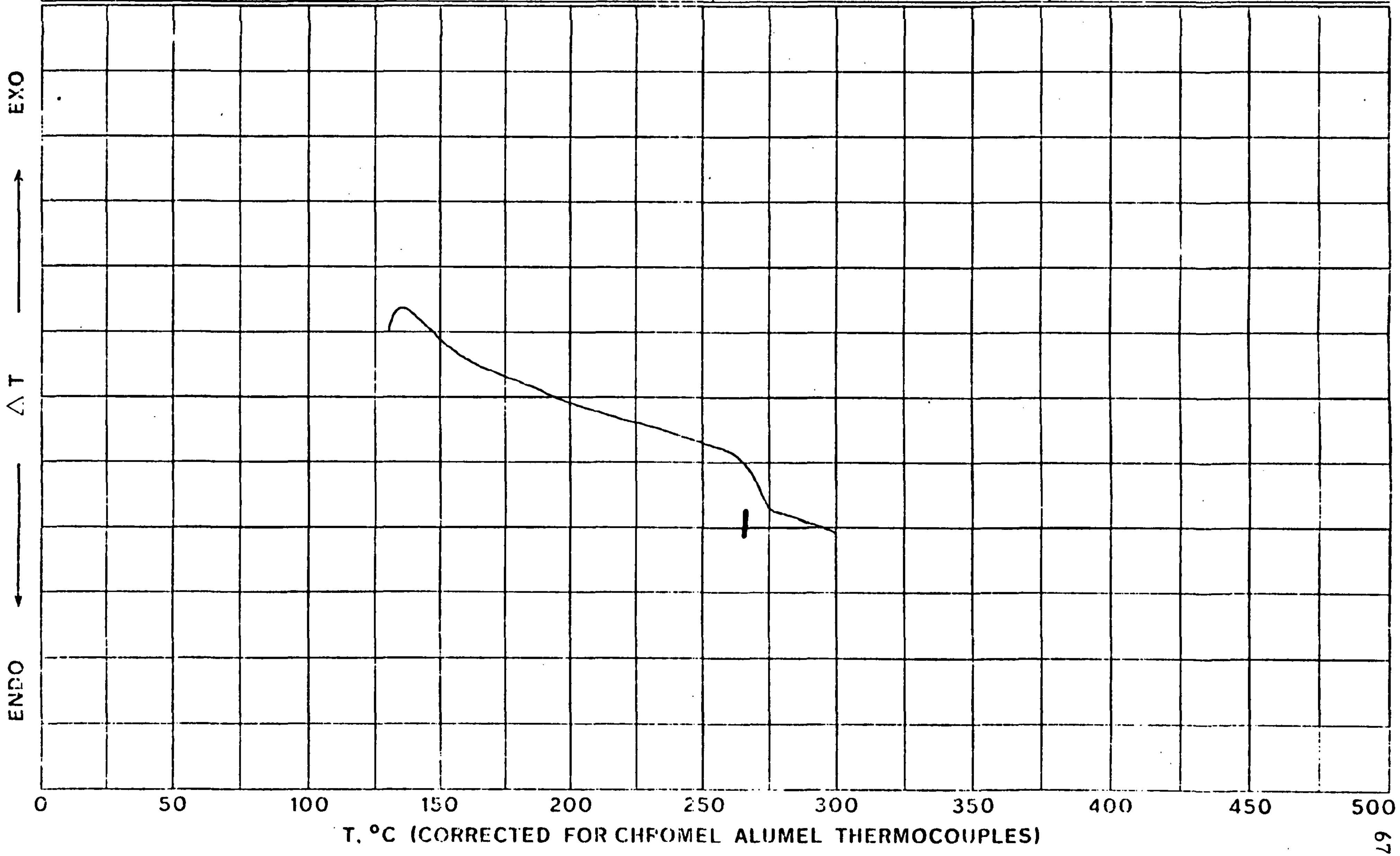
Appendix II
Figure 14
Phenolphthalein Polycarbonate
T_g 264° (via DTA)

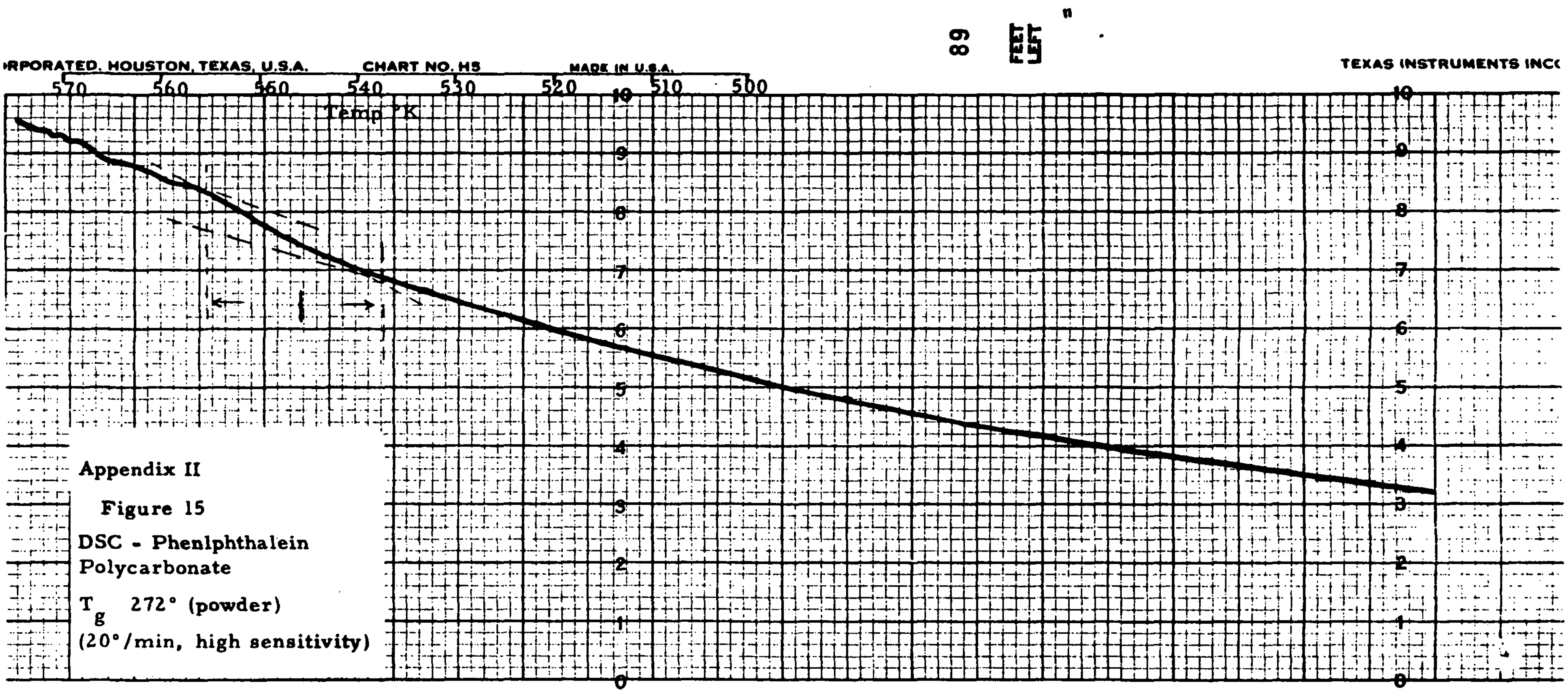
SIZE Micro
REF. Beads
PROGRAM MODE
RATE 30 °C/MIN .START °C

ATM.

	T	ΔT
SCALE SETTING	50 °C/IN.	0.2 °C/IN.

RUN NO.
DATE 3/28/72
OPERATOR H.K.





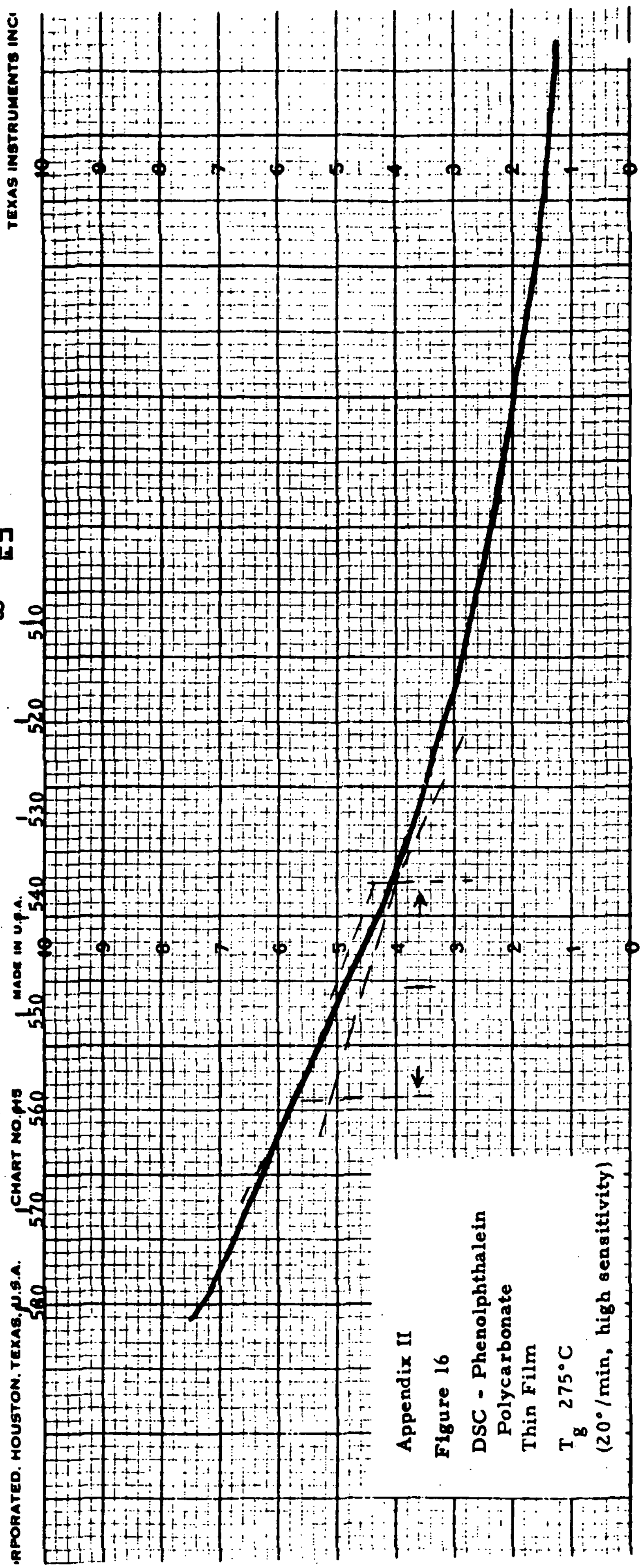
Appendix II

Figure 15

DSC - Phenlphthalein Polycarbonate

T_g 272° (powder)

(20°/min, high sensitivity)



Appendix II

Figure 16

DSC - Phenolphthalein Polycarbonate Thin Film

T_g 275°C

(20°/min, high sensitivity)

Appendix II
Figure 17
Phenolphthalein Polycarbonate
TGA (in air)
10 mg

X-AXIS

TEMP. SCALE 50 °C/inch

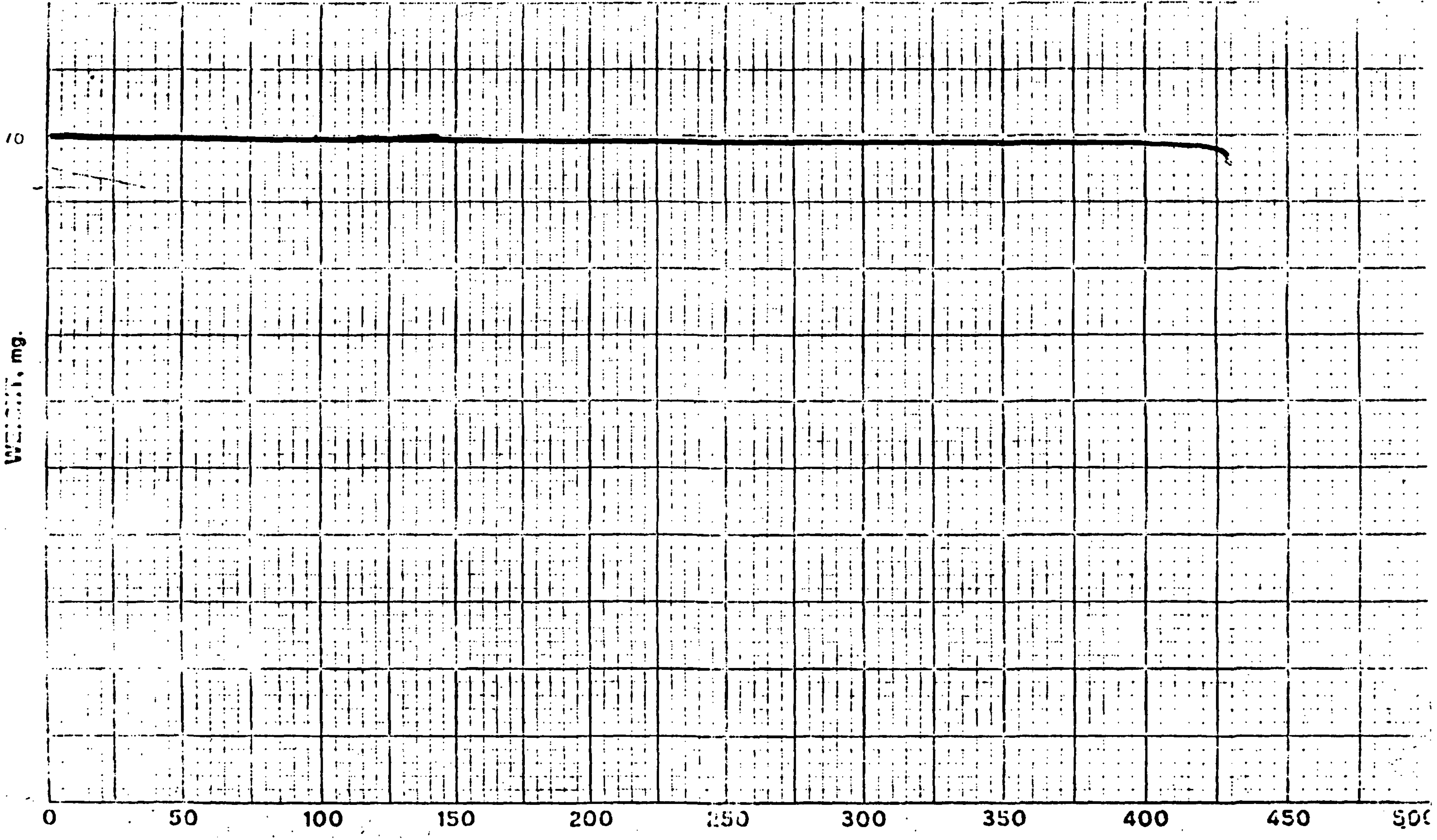
SHIFT 0 inch

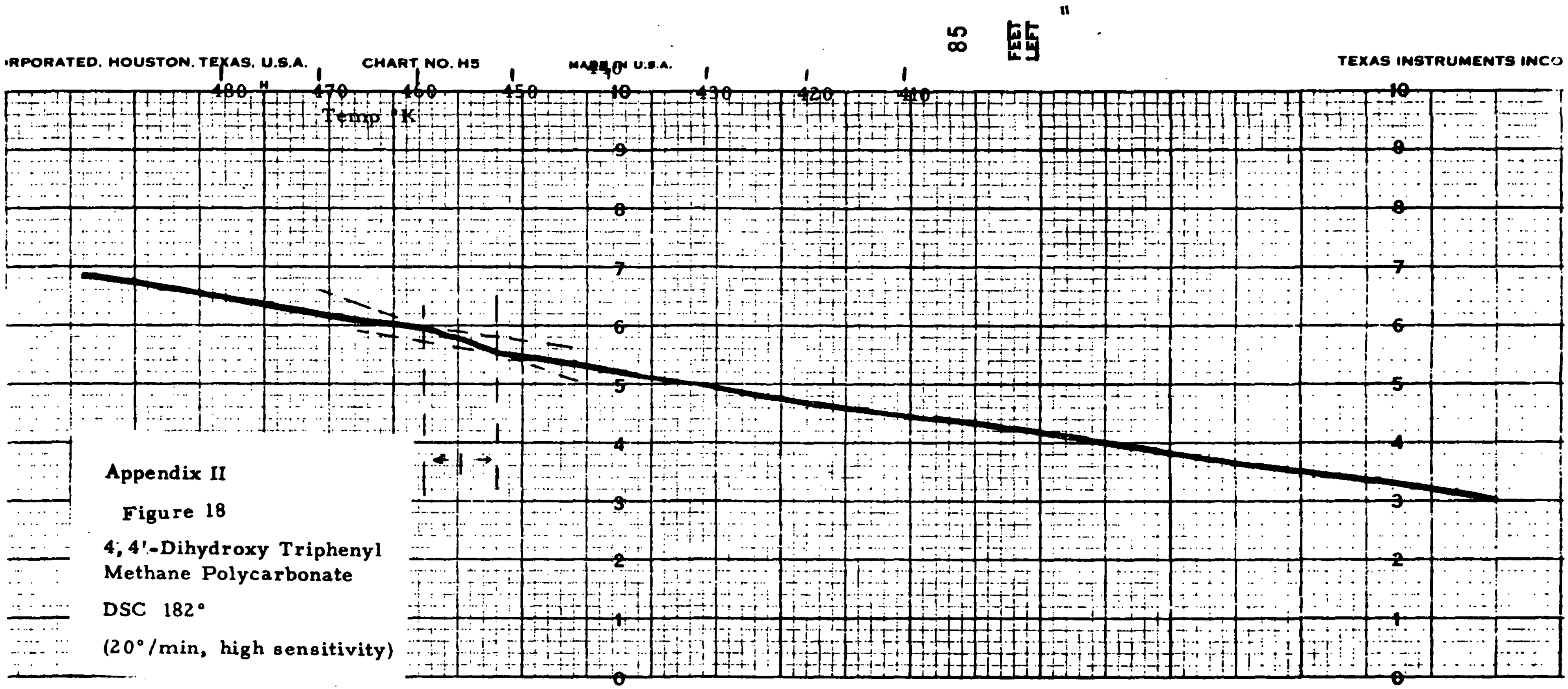
Y-AXIS

SCALE 2 mg./inch
(SCALE SETTING X 2)

SUPPRESSION 0 mg.

RUN NO. ____ DATE 10/26/71
OPERATOR ____
HEATING RATE 7°C min.
ATM. AIR (flowing)
TIME CONSTANT 2 sec.





Appendix II

Figure 18

4,4'-Dihydroxy Triphenyl Methane Polycarbonate

DSC 182°

(20°/min, high sensitivity)

Appendix II
Figure 19

4,4'-Dihydroxy Triphenyl Methane Polycarbonate

TGA (in air) 11.5 mg

X-AXIS

TEMP. SCALE ____ °C/inch

SHIFT ____ inch

TIME SCALE (ALT.) ____

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 0 mg.

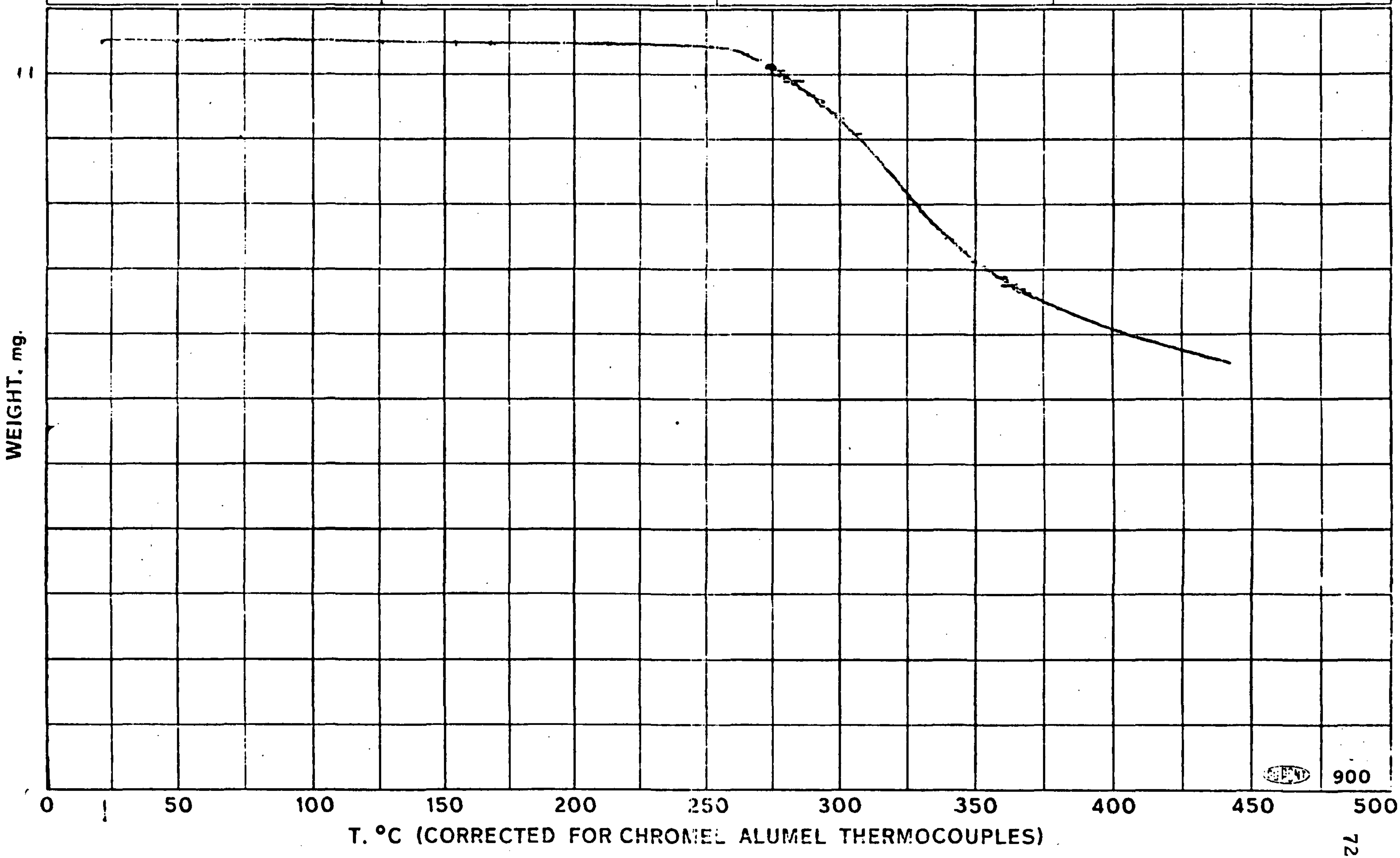
RUN NO. ____ DATE 5/12/7

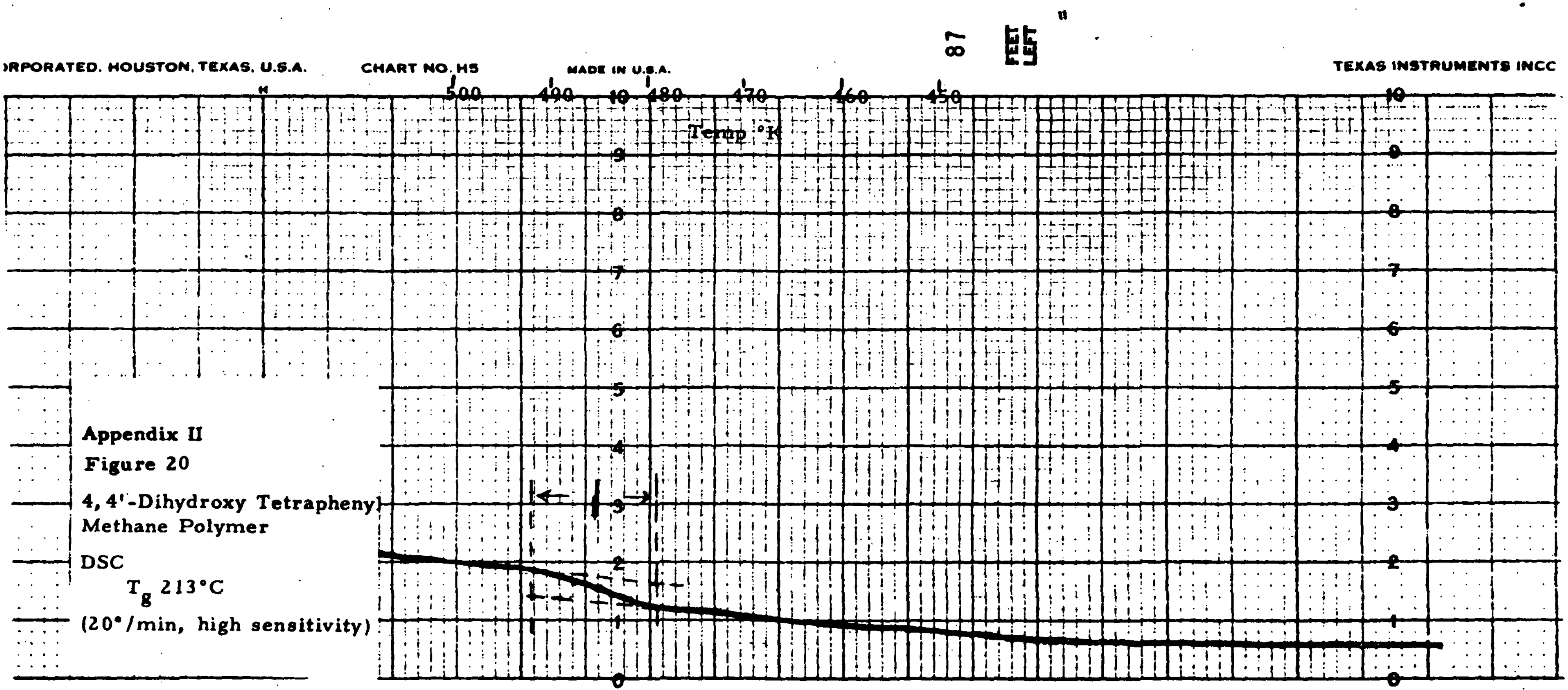
OPERATOR ECF

HEATING RATE 7 °C/min.

ATM. air

TIME CONSTANT 2 sec.



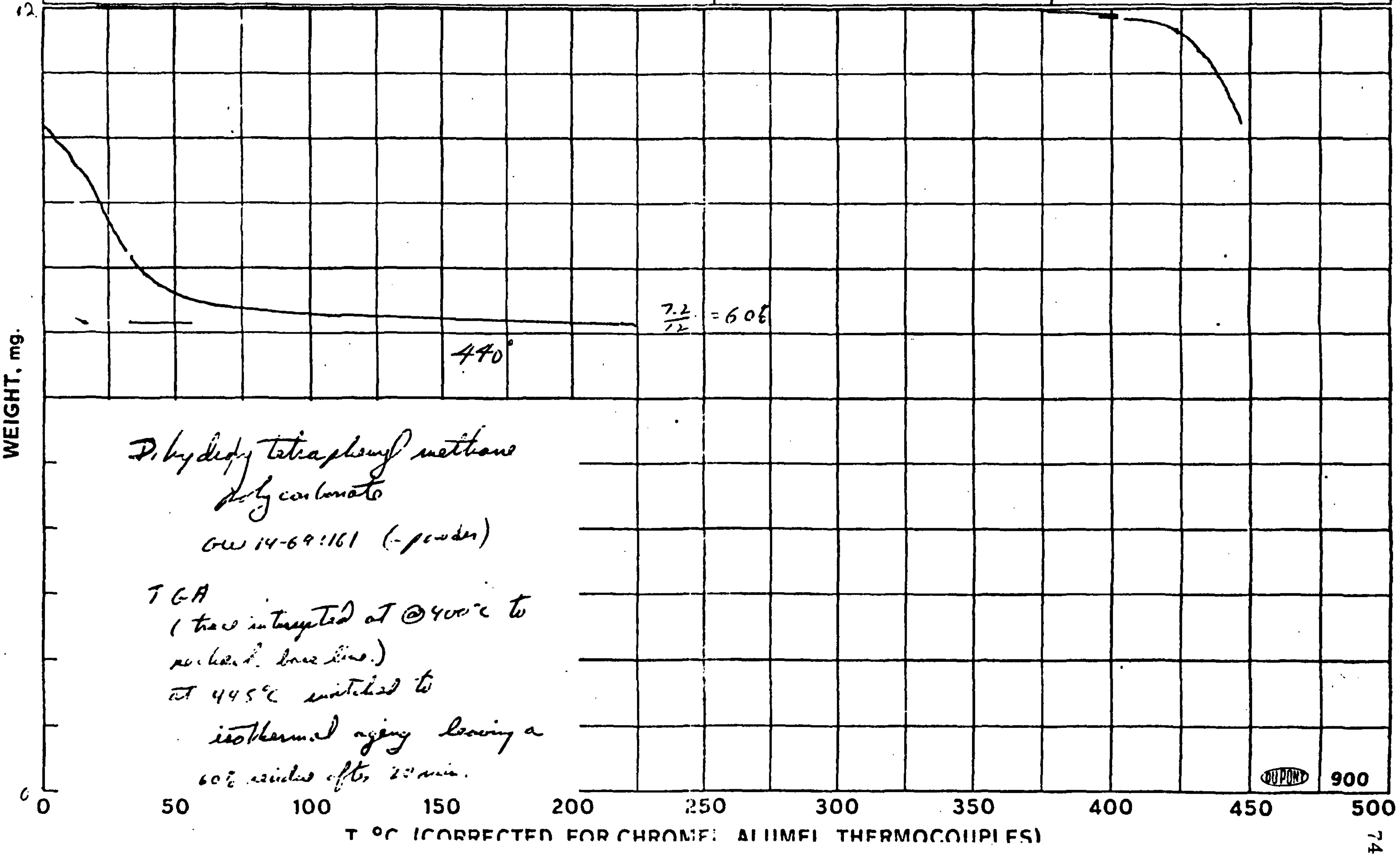


Appendix II
Figure 20
4, 4'-Dihydroxy Tetraphenyl Methane Polymer
DSC
T_g 213°C
(20°/min, high sensitivity)

Appendix II
Figure 21

TGA (in air) 12 mg
TiT_6

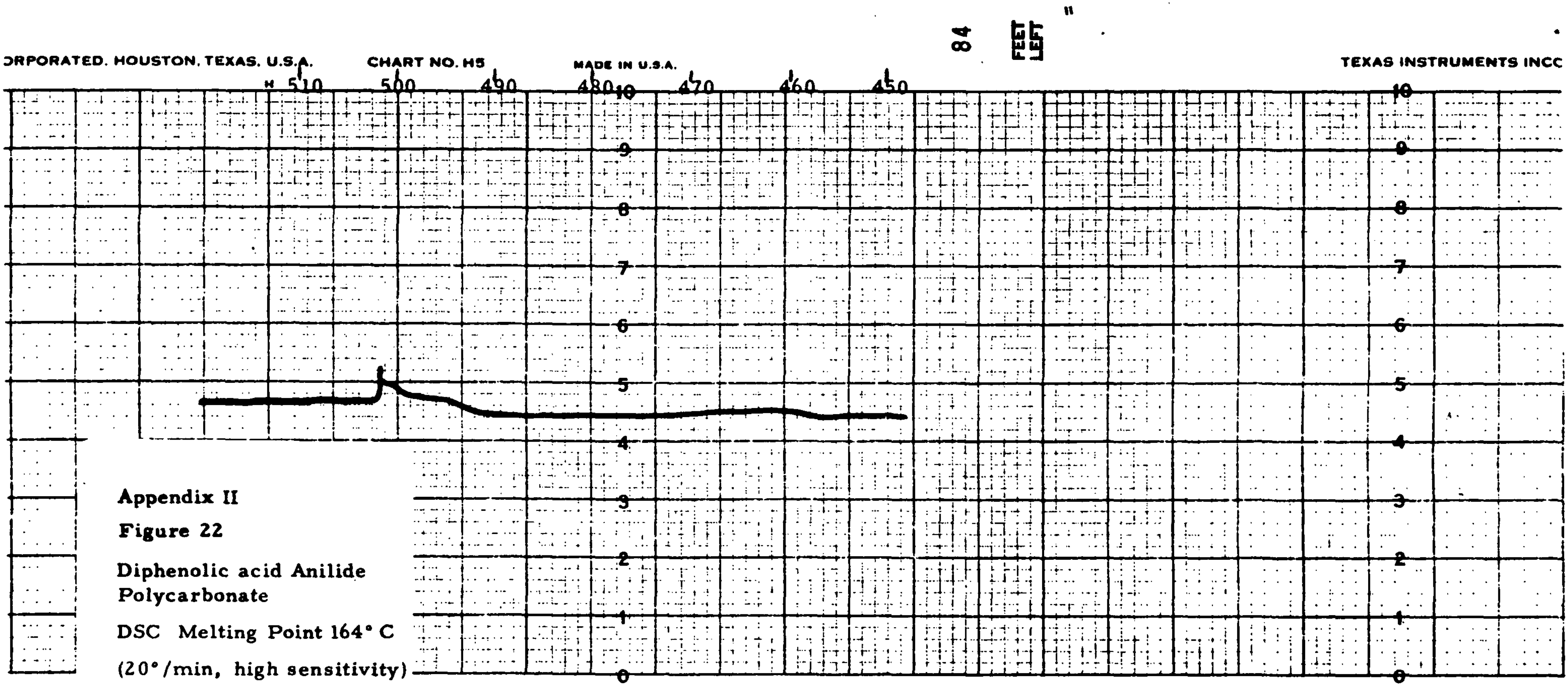
SAMPLE:	X-AXIS	Y-AXIS	
	EMP. SCALE 50 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	RUN NO. ____ DATE ____
	HIFT ____ inch		OPERATOR CK
	ME SCALE (ALT.) .5 in/inch	SUPPRESSION 0 mg.	HEATING RATE 7 °C/min.
			ATM. AIR
			TIME CONSTANT 2 sec.



Dihydroxy tetraphenyl methane
polycarbonate

GW 14-69:161 (-powder)

TGA
(trace interrupted at @400°C to
recheck base line.)
at 445°C switched to
isothermal aging leaving a
60% residue after 20 min.



Appendix II

Figure 22

Diphenolic acid Anilide
Polycarbonate

DSC Melting Point 164° C

(20°/min, high sensitivity)

Appendix II
Figure 23

Diphenolic Acid Anilide Polycarbonate

TGA (in air) 19.2 mg.

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 10 mg.

RUN NO.

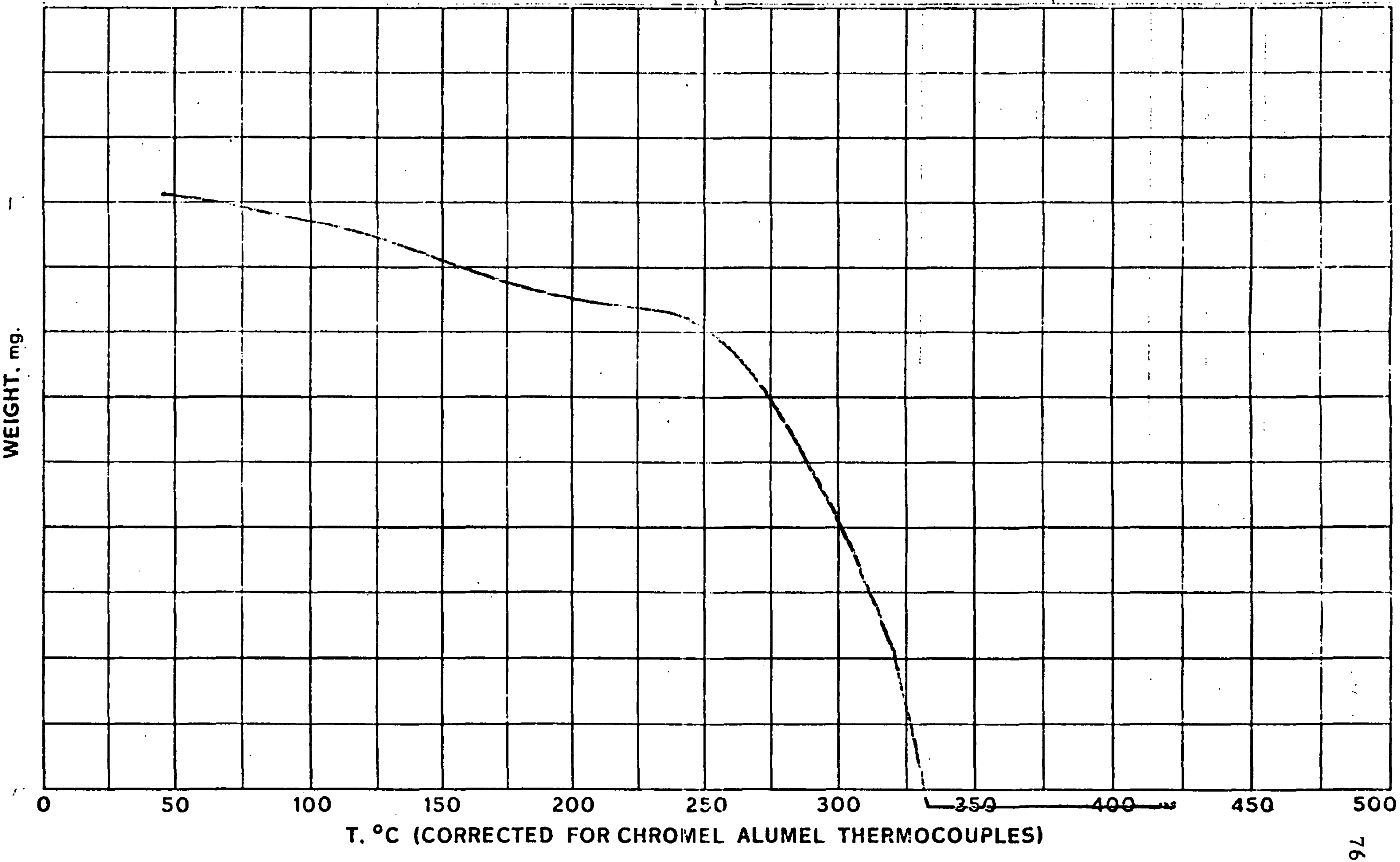
DATE 5/13/[illegible]

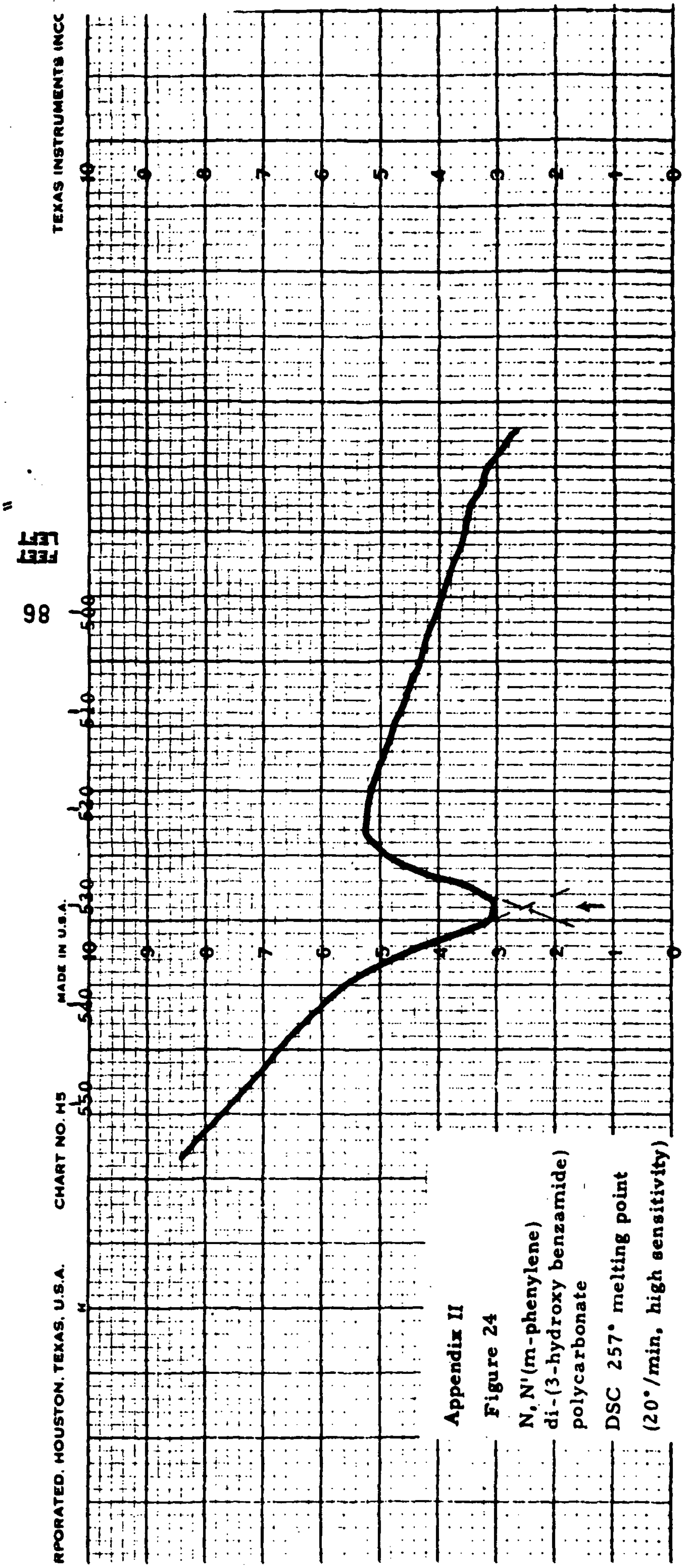
OPERATOR [illegible]

HEATING RATE 7 °C/min.

ATM. Air

TIME CONSTANT 1 sec.



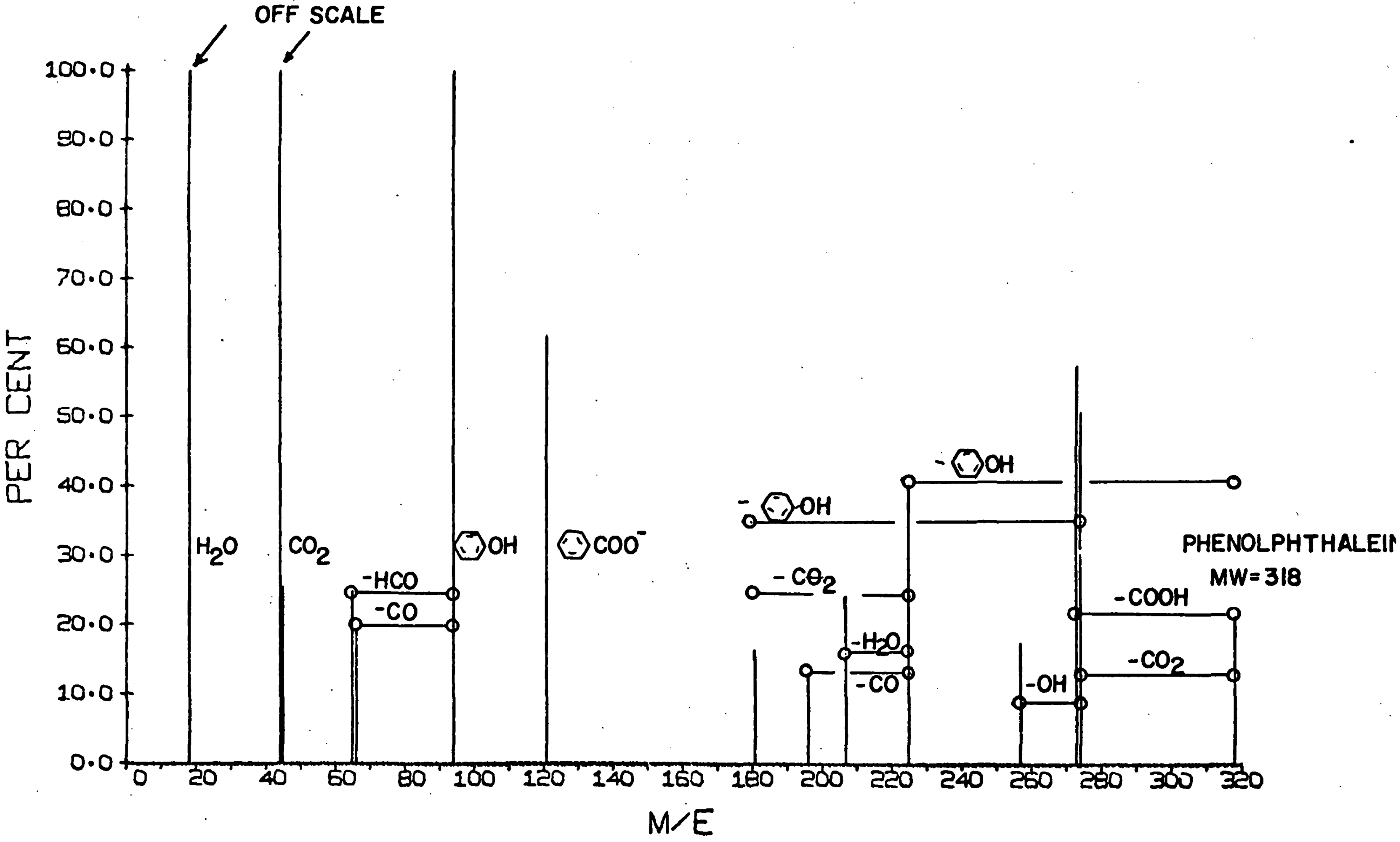


Appendix II

Figure 24

N, N'(m-phenylene)
di-(3-hydroxy benzamide)
polycarbonate

DSC 257° melting point
(20°/min, high sensitivity)



Appendix I$_I$
Figure 25

Mass Spectrum of Phenolphthalein Polycarbonate

(Determined by thermally fragmenting the polymer
in a vacuum. Phenolphthalein monomer could furnish a similar pattern.)

DU PONT INSTRUMENTS

Figure 26

Phenolphthalein Polycarbonate

Plant Run No. 1

23.6 mg (12 mg. suppression)

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 12 mg.

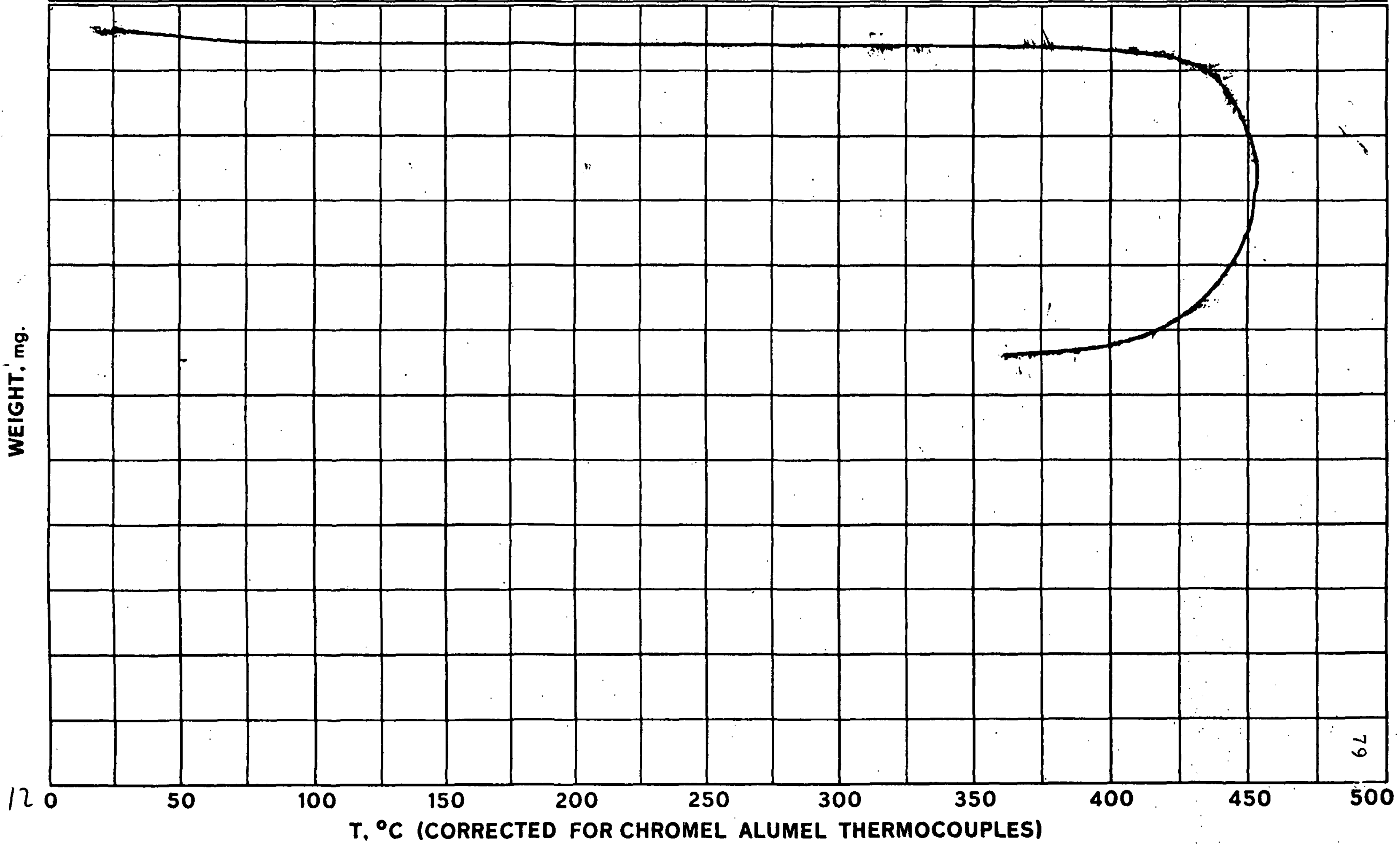
RUN NO. ____ DATE 7/1/72

OPERATOR ____

HEATING RATE 15 °C/min.

ATM. Air

TIME CONSTANT 1 sec.



DUPONT INSTRUMENTS

Figure 27

Plant Run No. 2

15.08 mg (10 mg. suppression)

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

Y-AXIS

SCALE 1 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 10 mg.

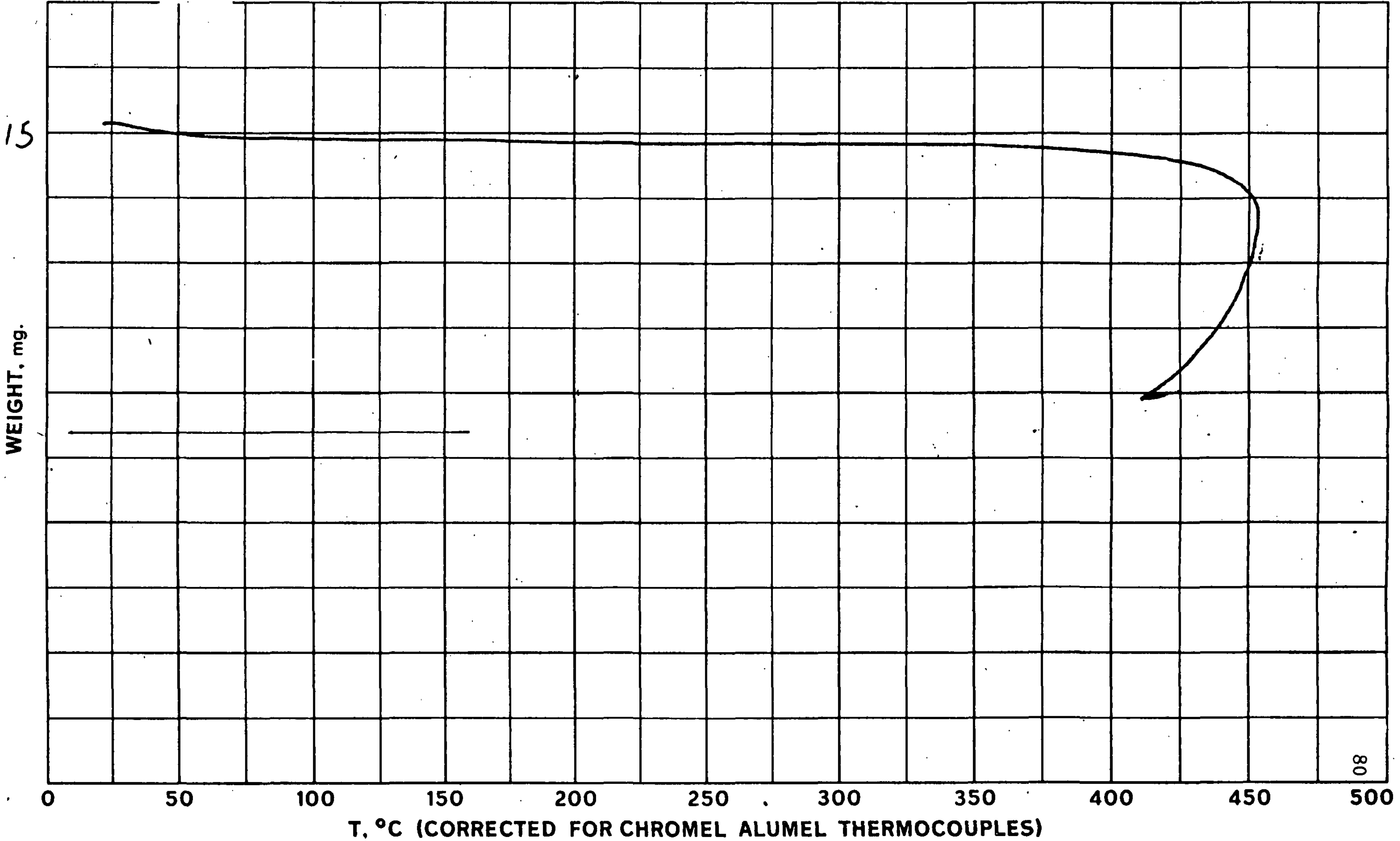
RUN NO. ____ DATE 7/6/72

OPERATOR HK

HEATING RATE 15 °C/min.

ATM. AIR

TIME CONSTANT 1 sec.



DUPONT INSTRUMENTS

Figure 28

Plant Run No. 3

20.3 mg. (10 mg. suppression)

X-AXIS

SCALE 50 °C/inch

0 inch

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 10 mg.

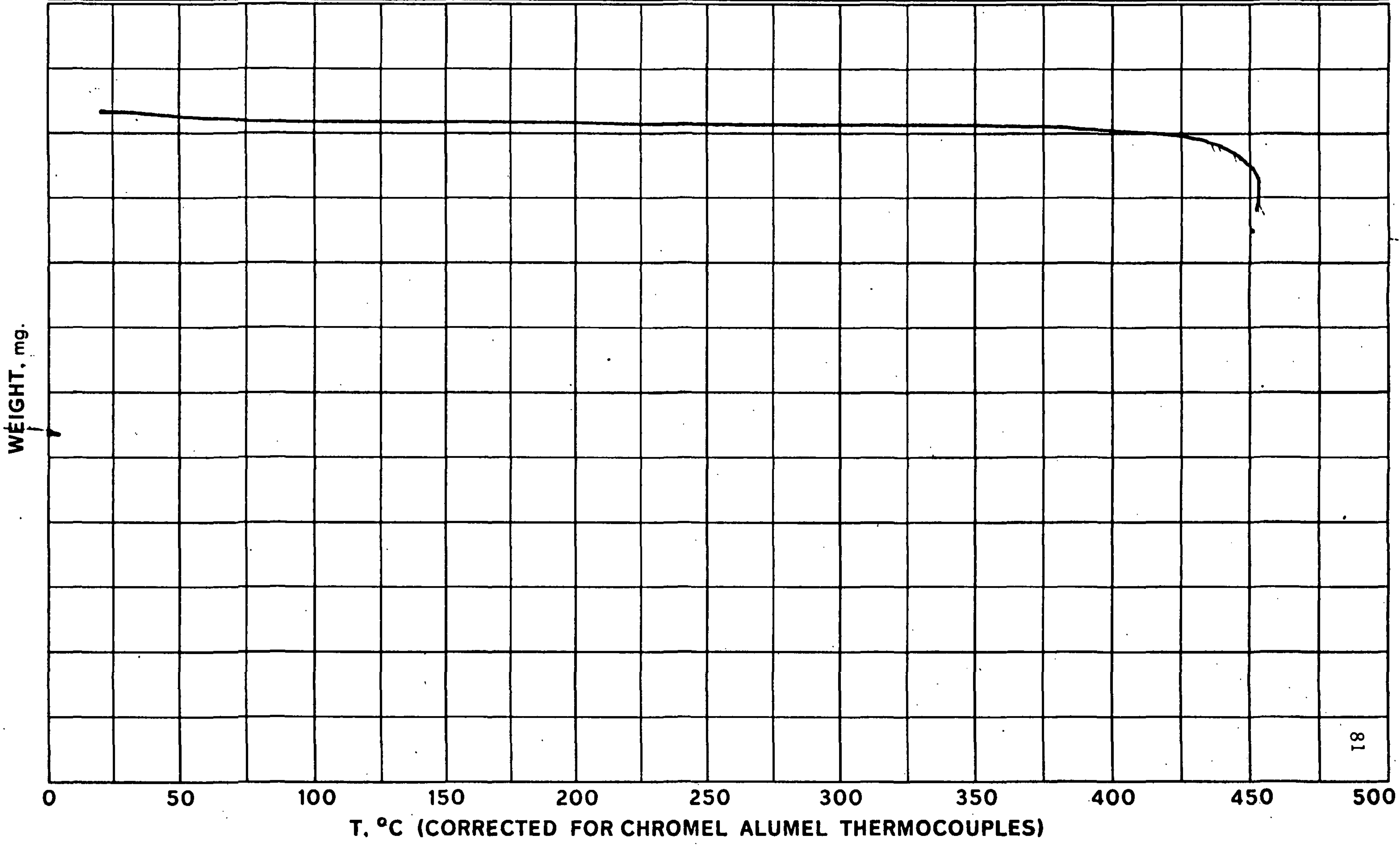
RUN NO. ____ DATE 7/6/72

OPERATOR ECF

HEATING RATE 15 °C/min.

ATM. air

TIME CONSTANT 1 sec.



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WILMINGTON, DELAWARE

SAMPLE:

Figure 29

Plant Run No. 4

17.65 mg. (10 mg. suppression)

X-AXIS

TEMP. SCALE ______ °C/inch

SHIFT ______ inch

TIME SCALE (ALT.) ______

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 10 mg.

RUN NO. ______ DATE 7/14/72

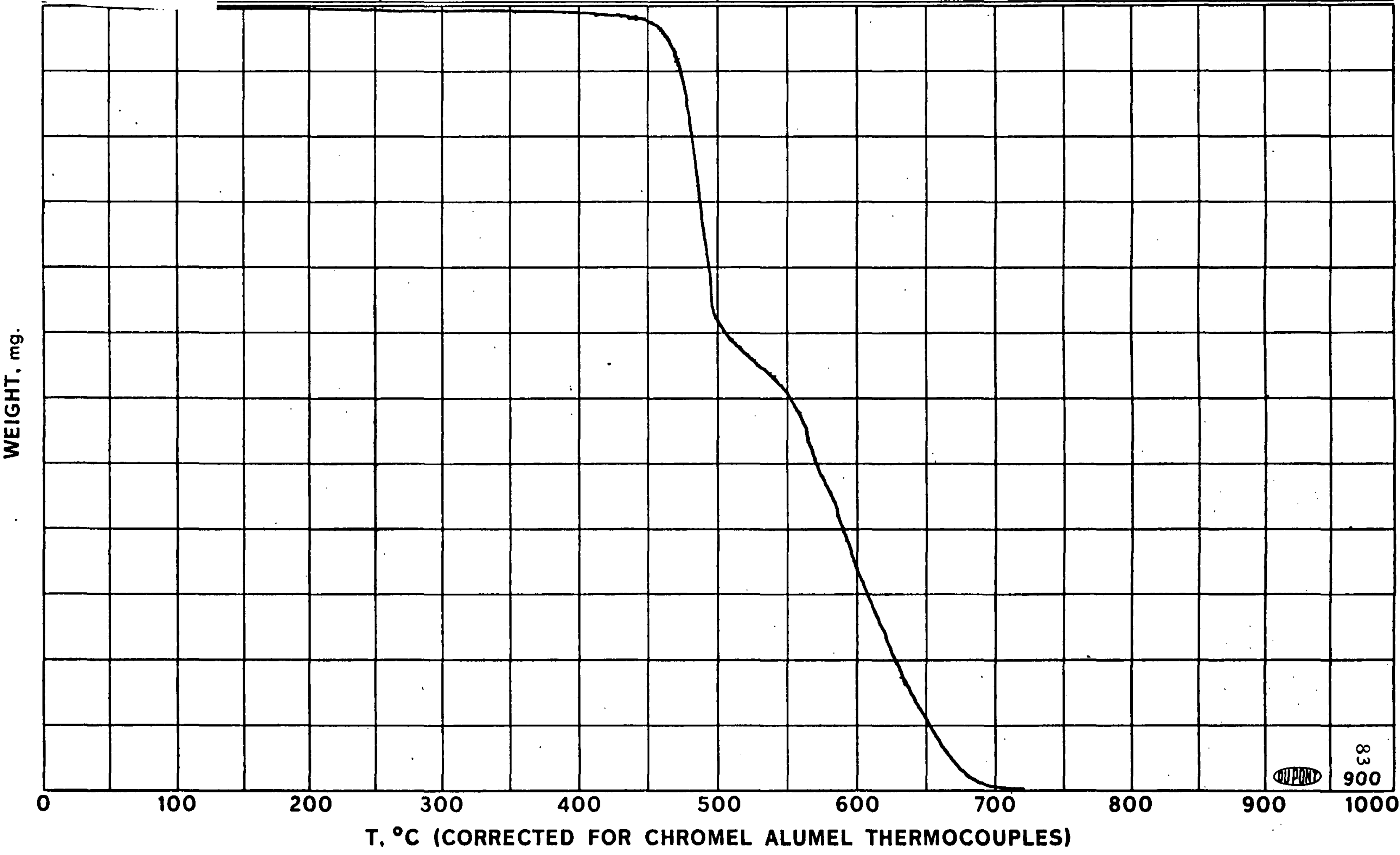
OPERATOR HK

HEATING RATE 15 °C/min.

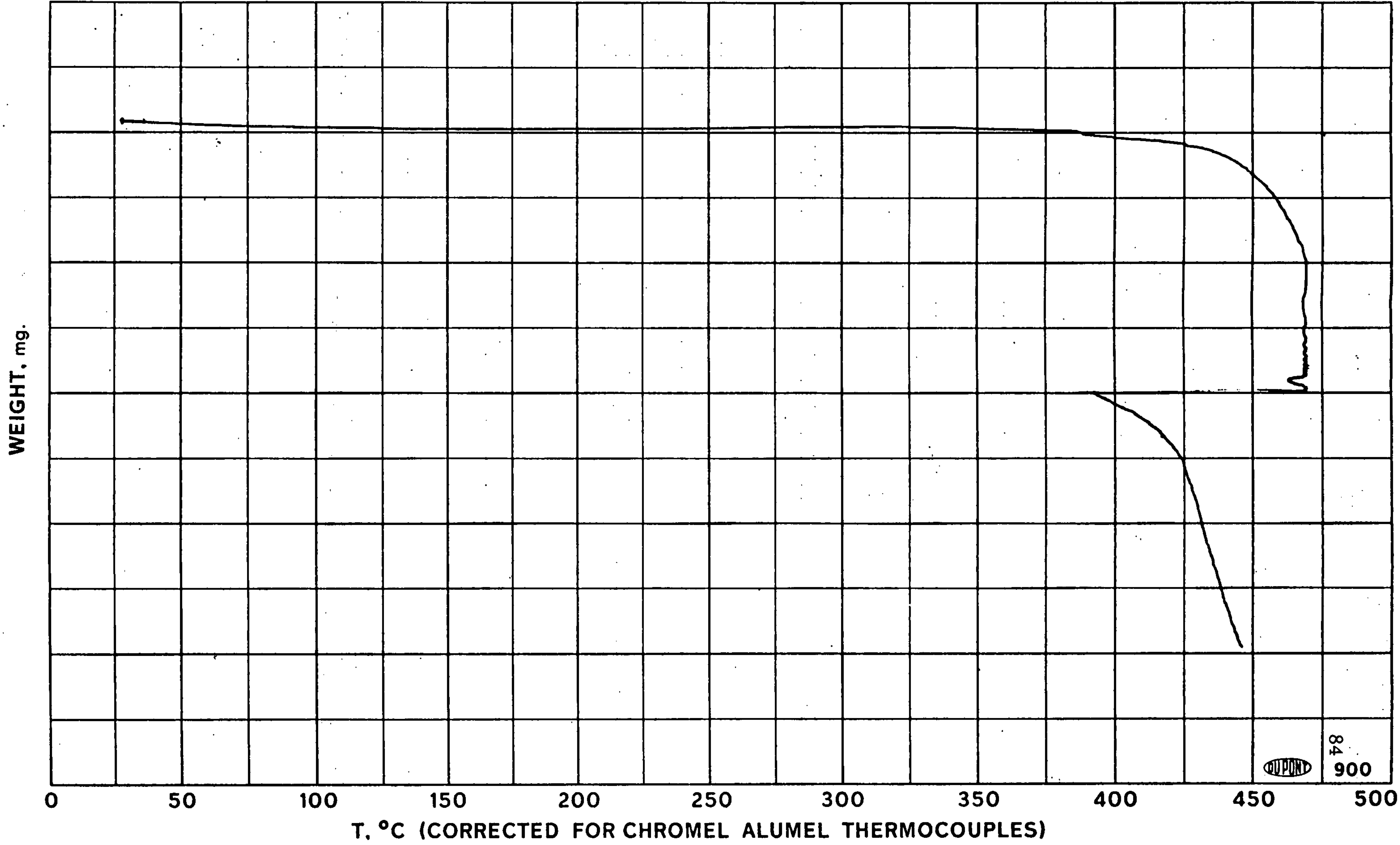
ATM. N2

TIME CONSTANT 1 sec.

SAMPLE:	**X-AXIS**	**Y-AXIS**	**RUN NO.** ____ **DATE** 7/27/72
Figure 30	**TEMP. SCALE** ____ °C/inch	**SCALE** 1 mg./inch	**OPERATOR** ____
Plant Run No. 5	**SHIFT** ____ inch	(SCALE SETTING X 2)	**HEATING RATE** 15 °C/min.
6 mg.	**TIME SCALE (ALT.)** ____	**SUPPRESSION** 0 mg.	**ATM.** Air **TIME CONSTANT** 2 sec.



SAMPLE:	X-AXIS	Y-AXIS	RUN NO. ___ DATE 10/2/72
Figure 31	TEMP. SCALE ___ °C/inch	SCALE 2 mg./inch	OPERATOR ECF
Plant Run No. 6	SHIFT ___ inch	(SCALE SETTING X 2)	HEATING RATE 10 °C/min.
			ATM. air
SIZE 10.2 mg.	TIME SCALE (ALT.) ___	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



DU PONT INSTRUMENTS

SAMPLE:

Figure 32

Plant Run No. 7

SIZE 9.75 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 0 mg.

RUN NO. **DATE** 10/2/72

OPERATOR ECF

HEATING RATE 10 °C/min.

ATM. air

TIME CONSTANT 2 sec.

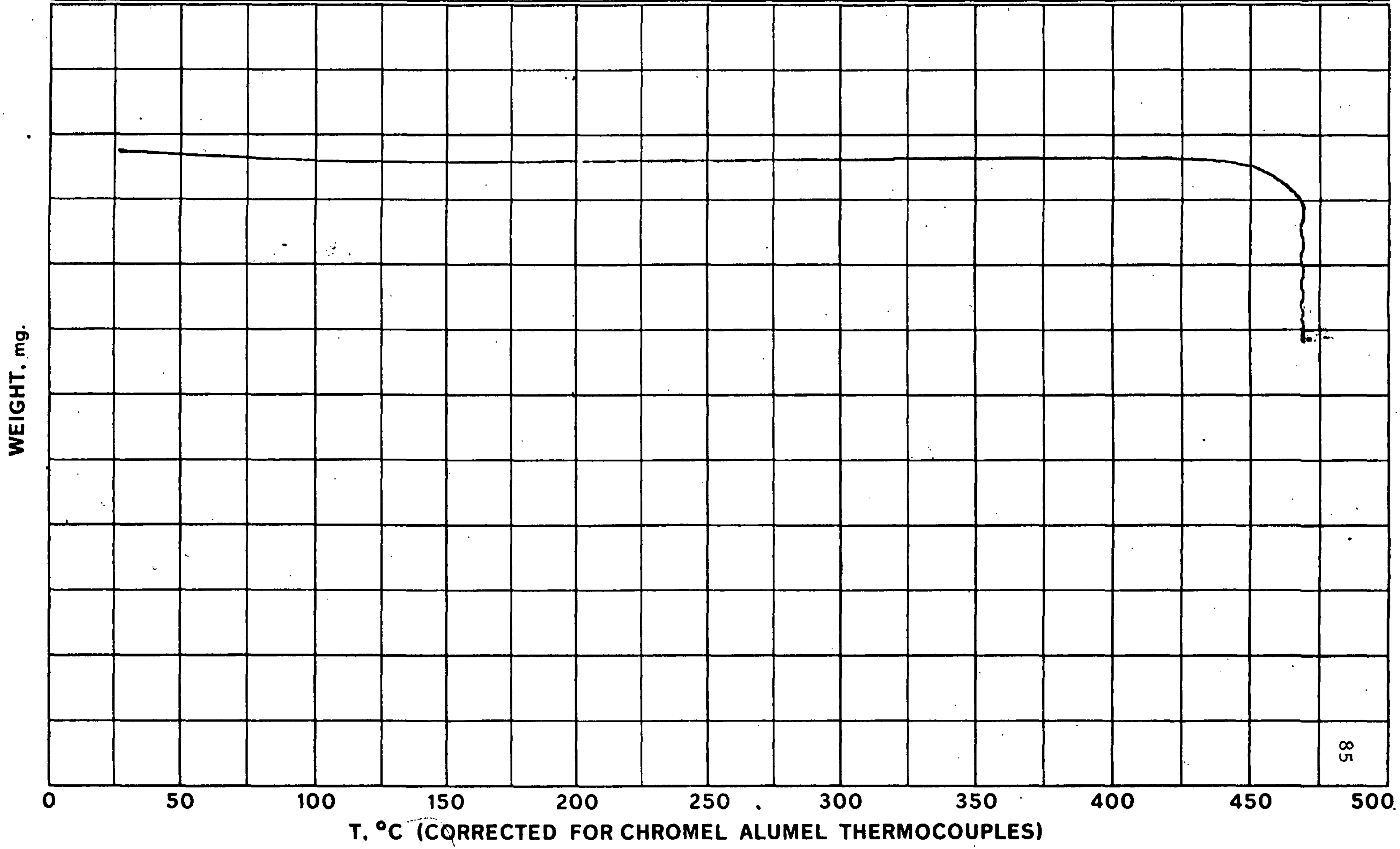
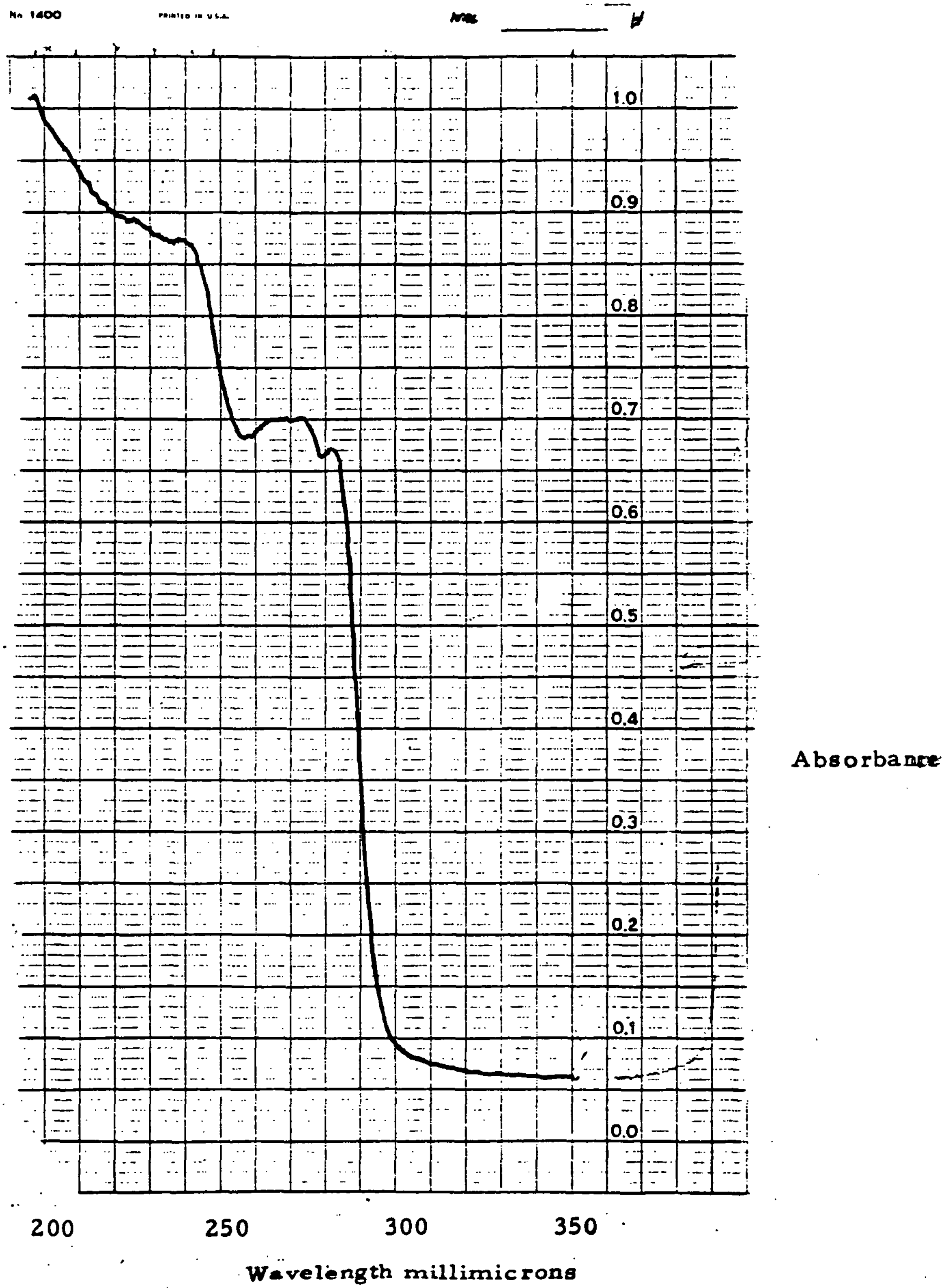


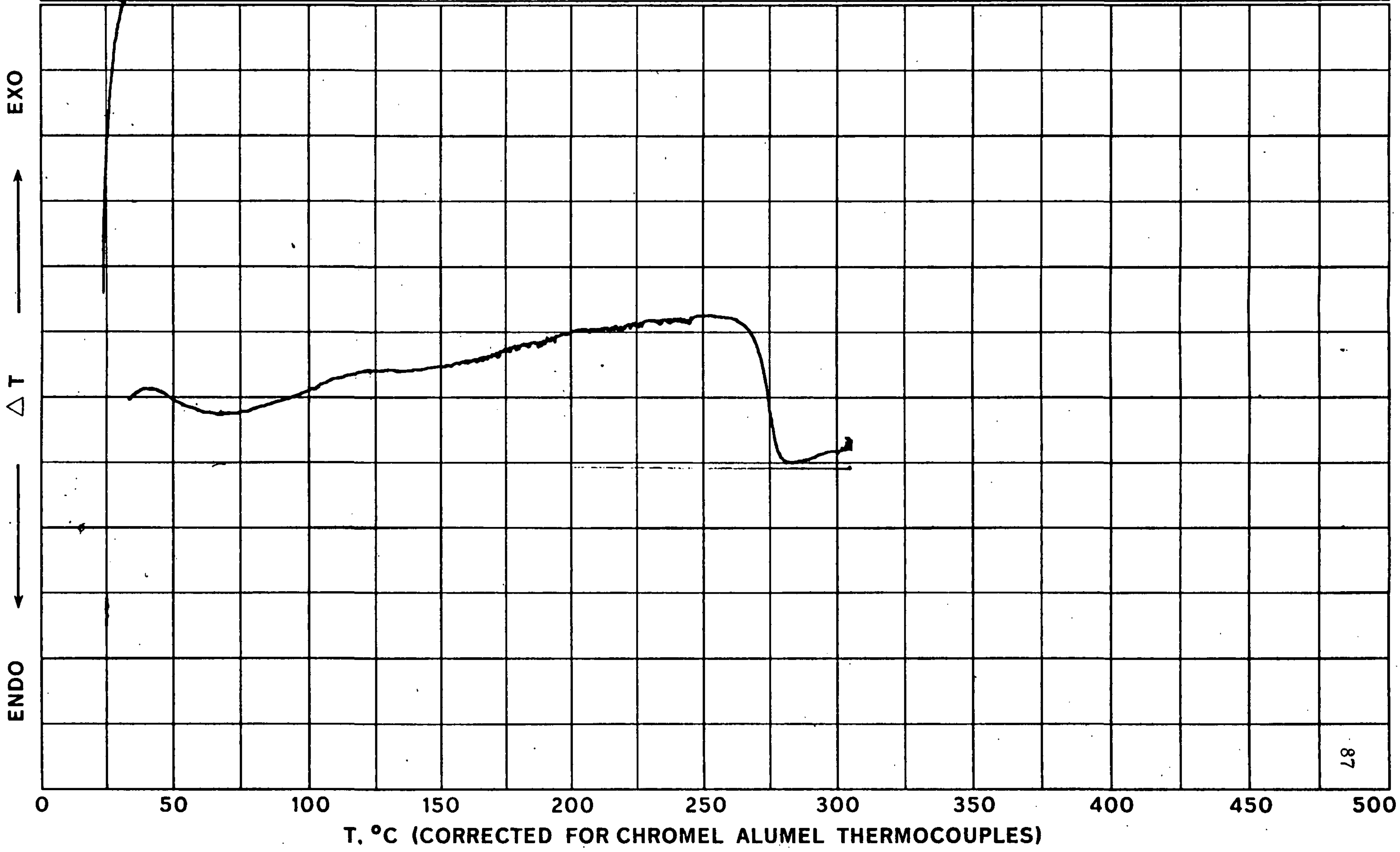
FIGURE 33

ULTRAVIOLET SPECTRUM PANEL NO. 5



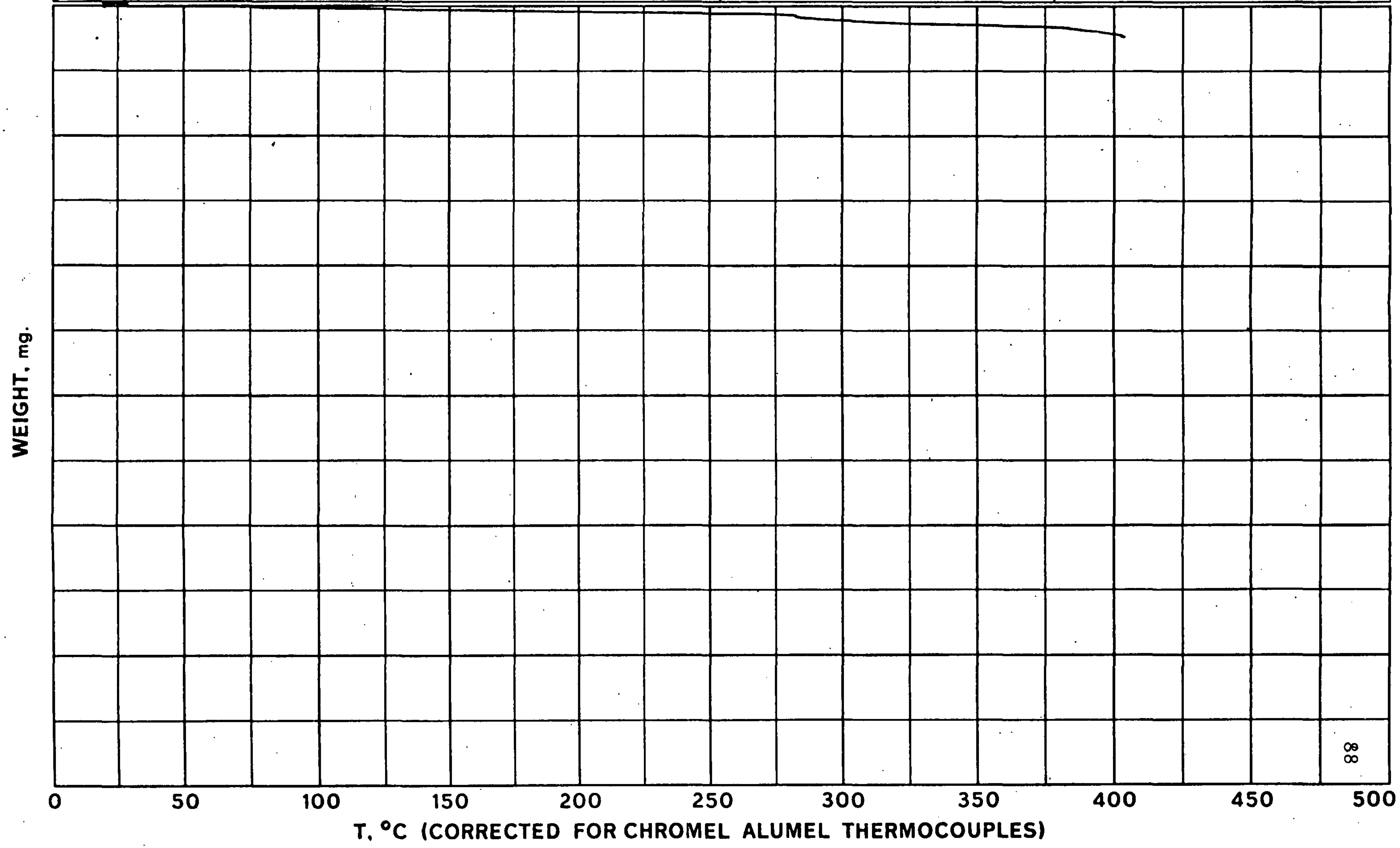
DU PONT INSTRUMENTS

SAMPLE: Figure 34 DTA Plant Run No. 1	SIZE Micro	ATM. AIR	RUN NO.
	REF.		DATE 7/12/72
	PROGRAM MODE	SCALE SETTING T 50 °C/IN. ΔT 0.2 °C/IN.	OPERATOR
ORIGIN:	RATE 30 °C/MIN, START °C		

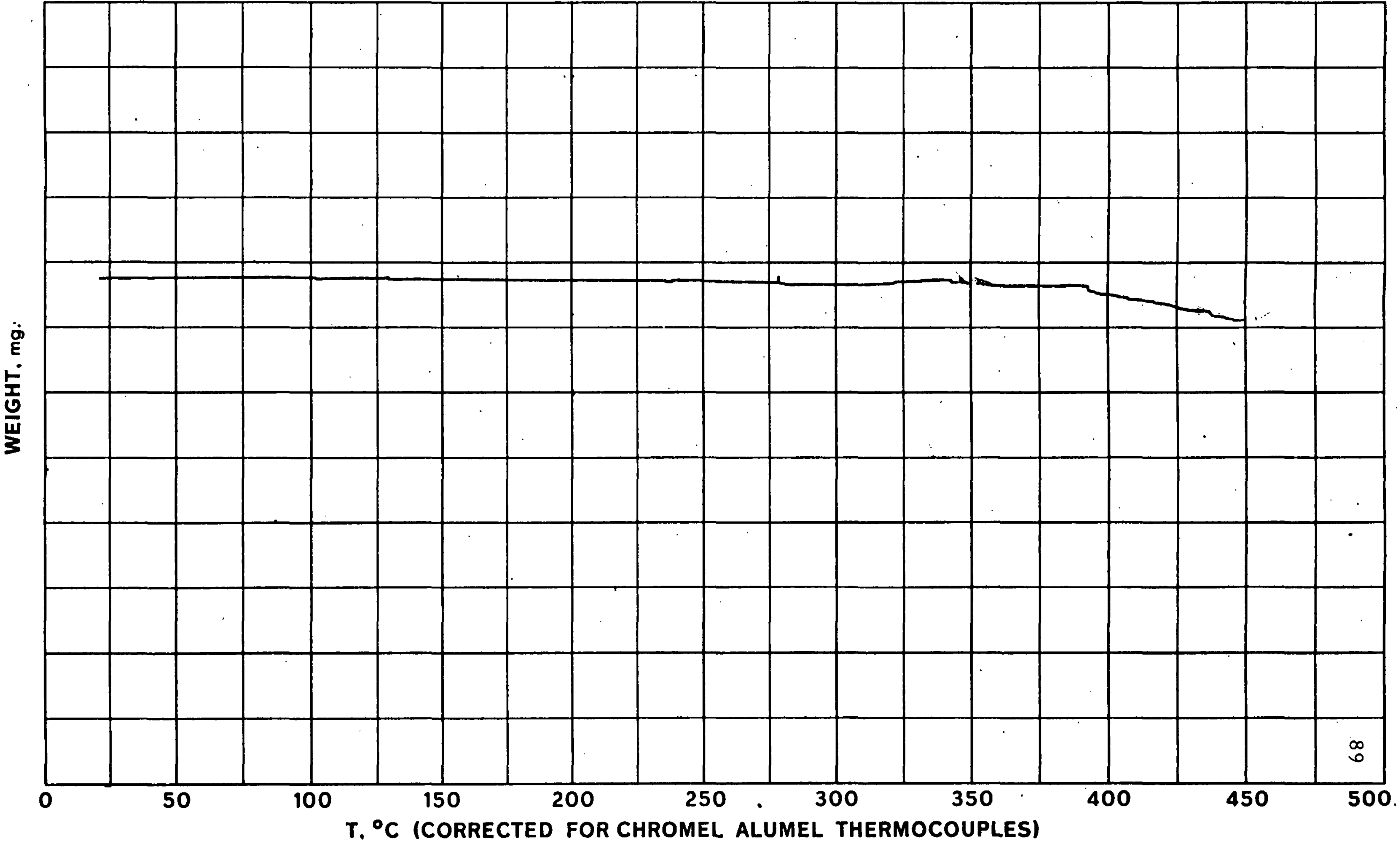


DU PONT INSTRUMENTS

SAMPLE: Figure 35 Panel No. 2 12 mg (No suppression)	**X-AXIS** **TEMP. SCALE** 50 °C/inch **SHIFT** 0 inch	**Y-AXIS** **SCALE** 2 mg./inch (SCALE SETTING X 2) **SUPPRESSION** 0 mg.	**RUN NO.** ____ **DATE** 12/28/72 **OPERATOR** HK **HEATING RATE** 15 °C/min. **ATM.** AIR **TIME CONSTANT** 5 sec.

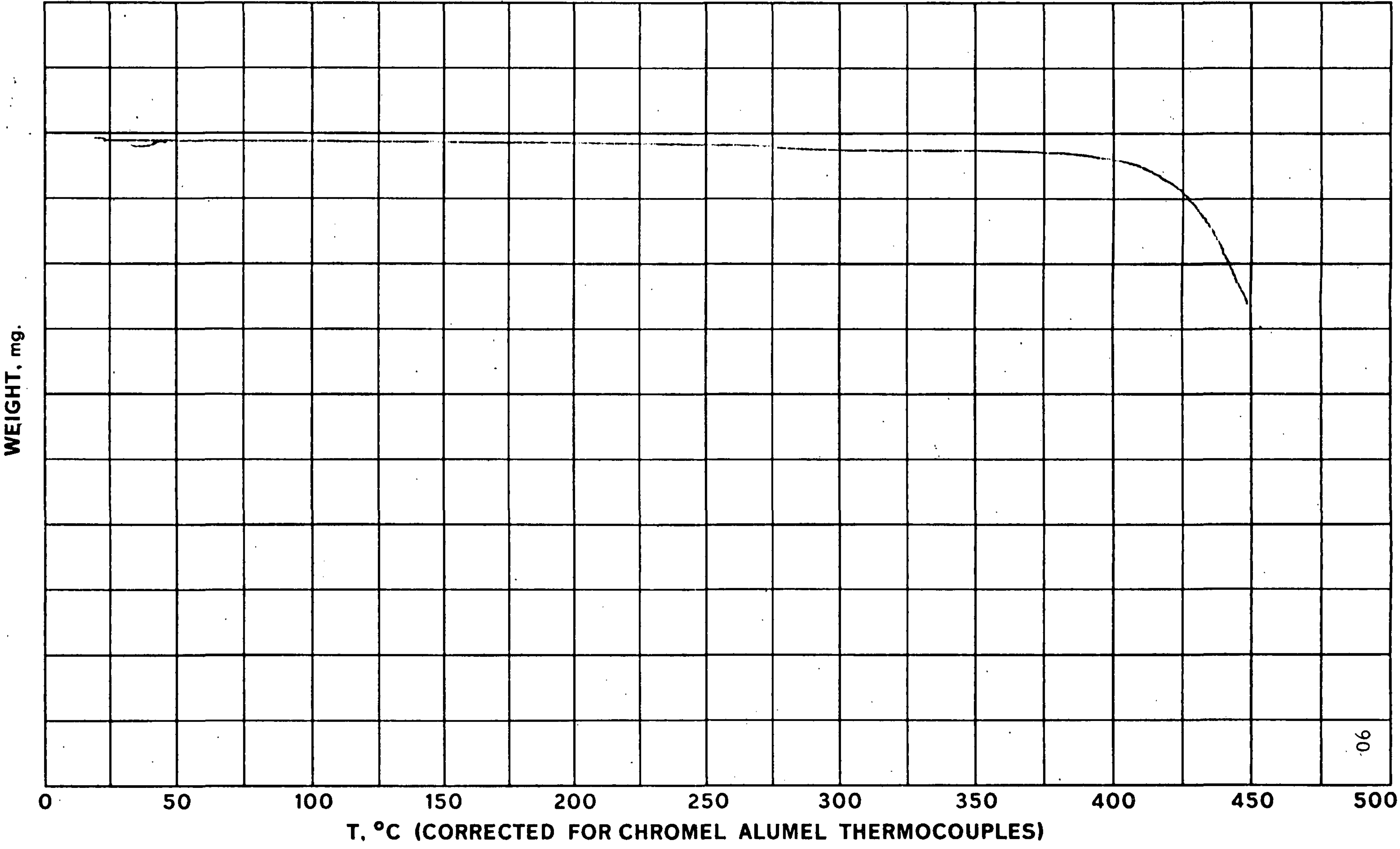


SAMPLE: Figure 36 Panel No. 3 7.72 mg (No suppression	X-AXIS TEMP. SCALE 50 °C/inch SHIFT 0 inch	Y-AXIS SCALE 2 mg./inch (SCALE SETTING X 2) SUPPRESSION 0 mg.	RUN NO. ____ DATE 11/4/72 OPERATOR ECF HEATING RATE 10 °C/min. ATM. air TIME CONSTANT 2 sec.



DU PONT INSTRUMENTS

SAMPLE: Figure 37 Panel No. 4 9.84 mg (No suppression)	**X-AXIS** TEMP. SCALE 50 °C/inch SHIFT 0 inch	**Y-AXIS** SCALE 2 mg./inch (SCALE SETTING X 2) SUPPRESSION 0 mg.	RUN NO. ____ DATE 12/14/77 OPERATOR ECF HEATING RATE 10 °C/min. ATM. air TIME CONSTANT 2 sec.



INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: –

Figure 38

Panel No. 5

10.8 mg (No suppression)

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT ______ inch

TIME SCALE (ALT.) ______

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 0 mg.

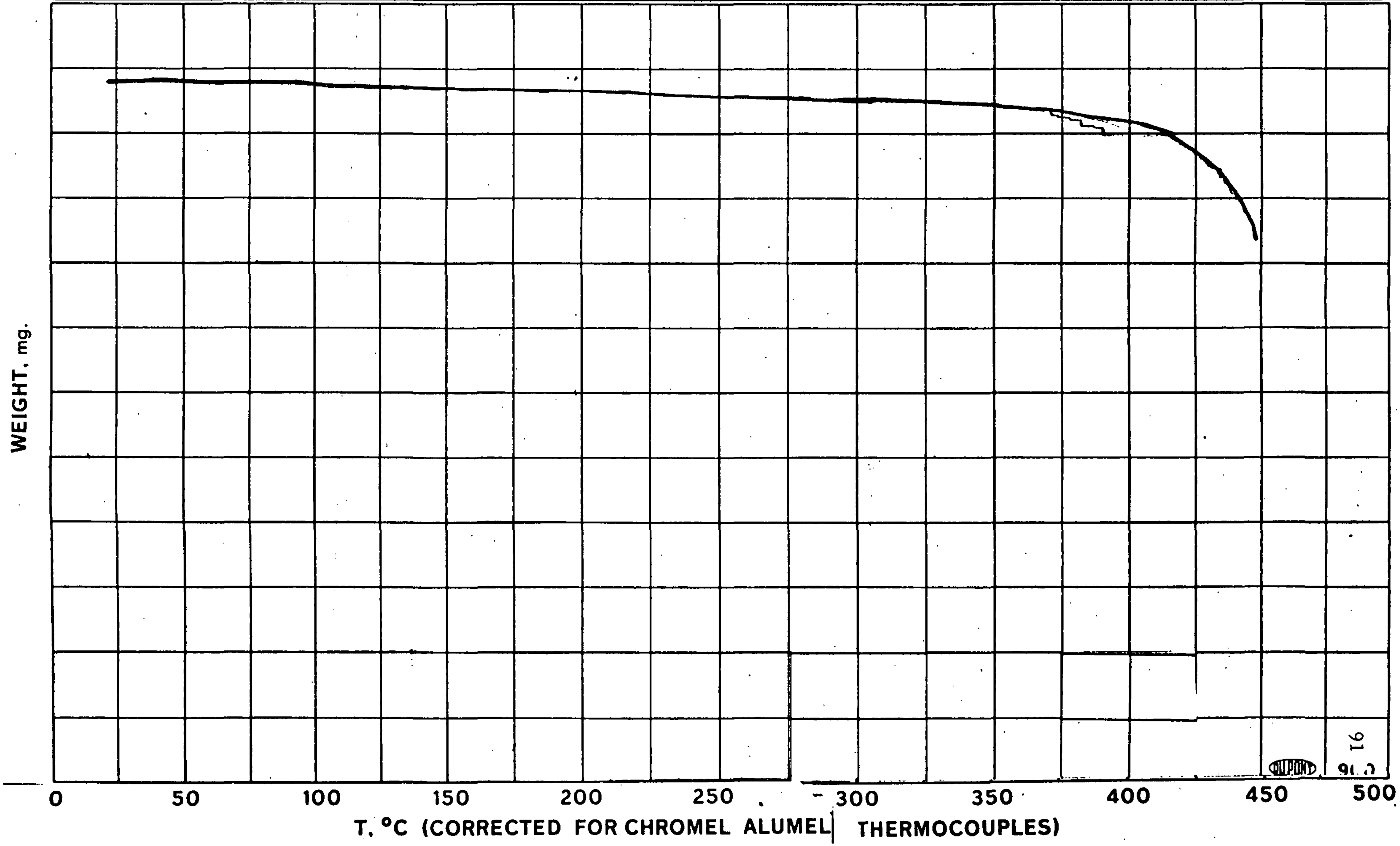
RUN NO. ______ **DATE** 12/14/72

OPERATOR ECF

HEATING RATE 10 °C/min.

ATM. air

TIME CONSTANT 2 sec.



DU PONT INSTRUMENTS

Figure 39

Panel No. 6

10.2 mg (No suppression)

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 0 mg.

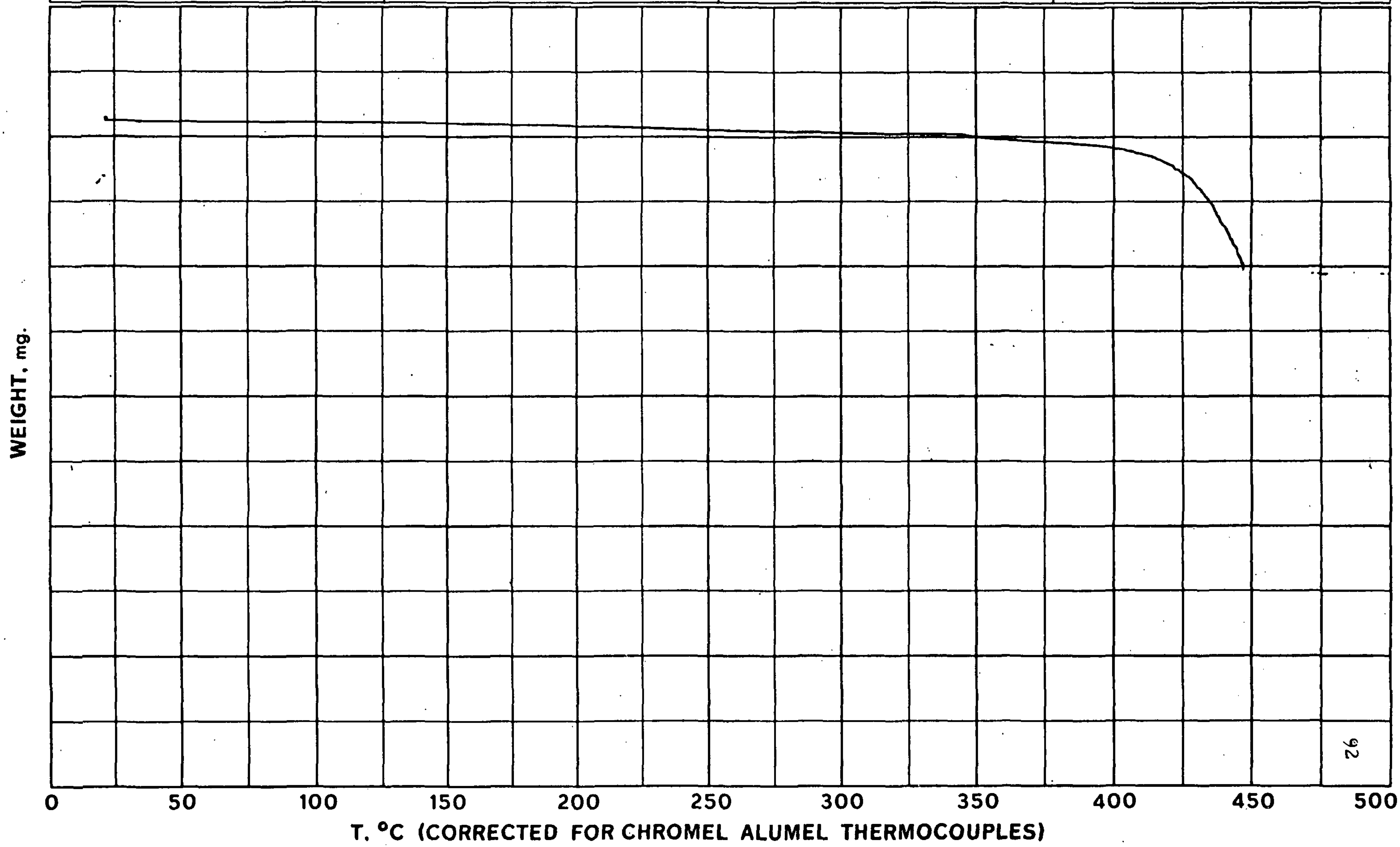
RUN NO. ____ DATE 12/18/72

OPERATOR ECF

HEATING RATE 10 °C/min.

ATM. air

TIME CONSTANT 2 sec.



DU PONT INSTRUMENTS

SAMPLE:

Figure 40

Panel No. 7

10.2 mg (No suppression)

X-AXIS

SCALE 50 °C/inch

SHIFT 0 inch

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 0 mg.

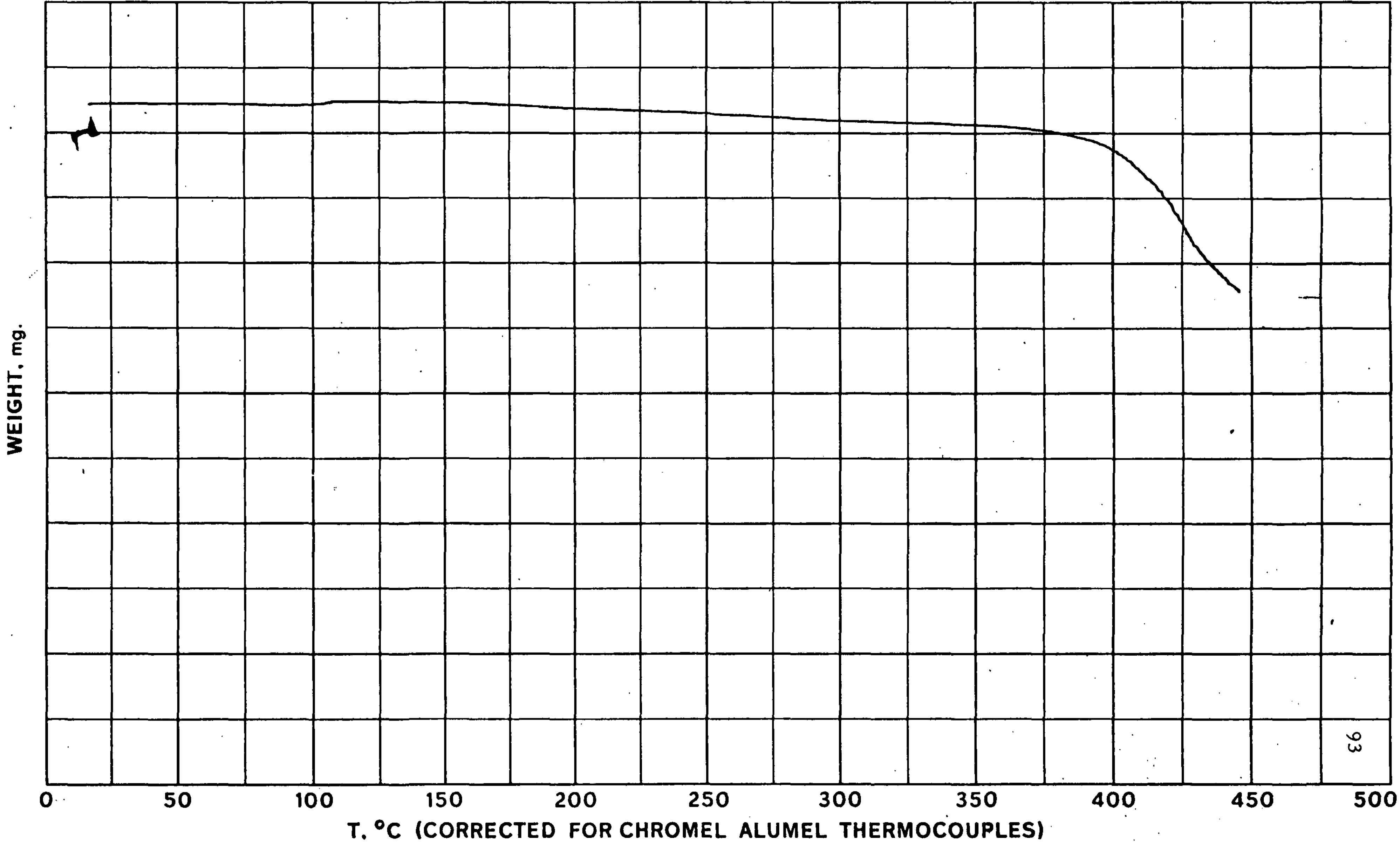
RUN NO. ______ DATE ______

OPERATOR SCF

HEATING RATE 10 °C/min.

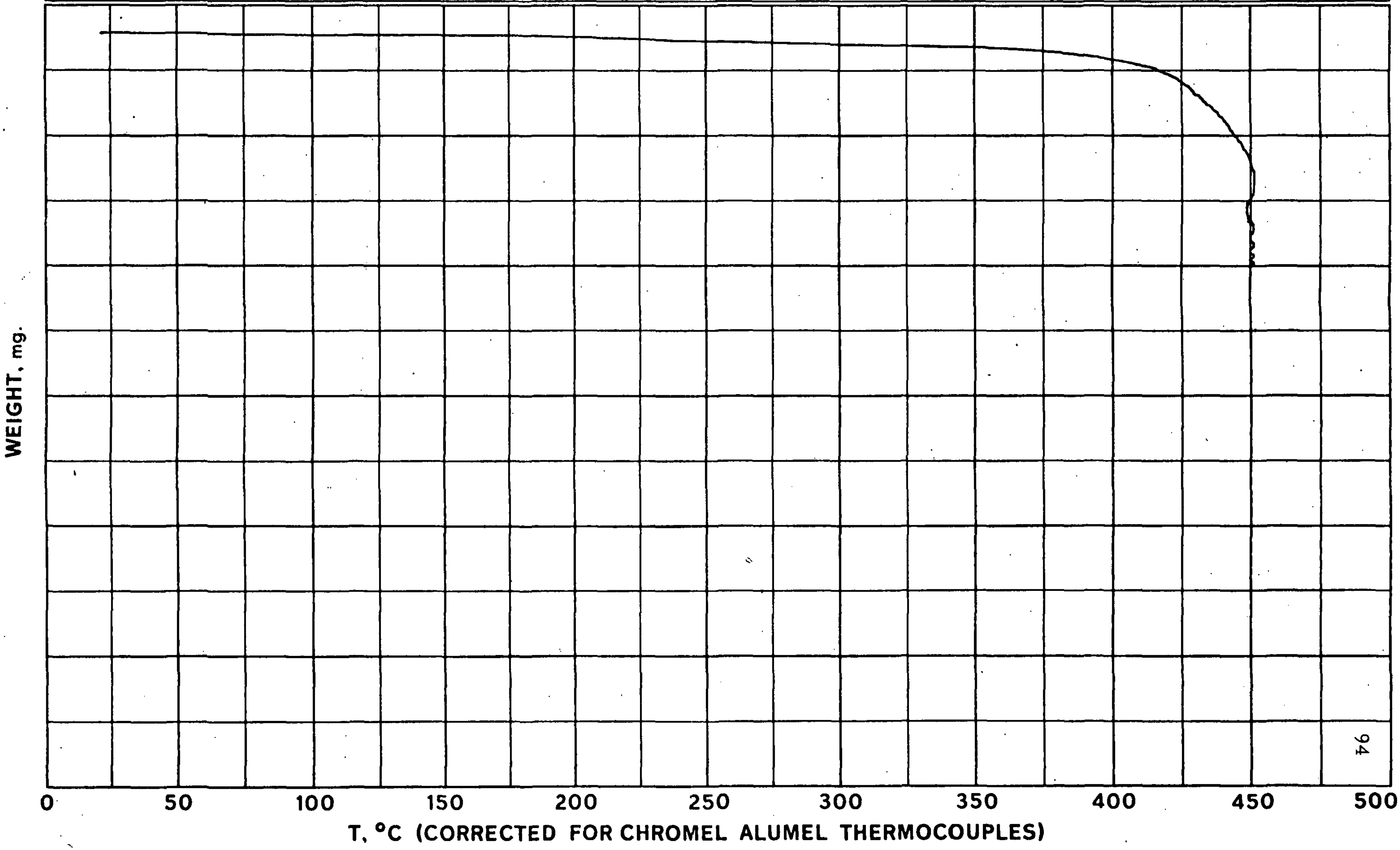
ATM. air

TIME CONSTANT 2 sec.



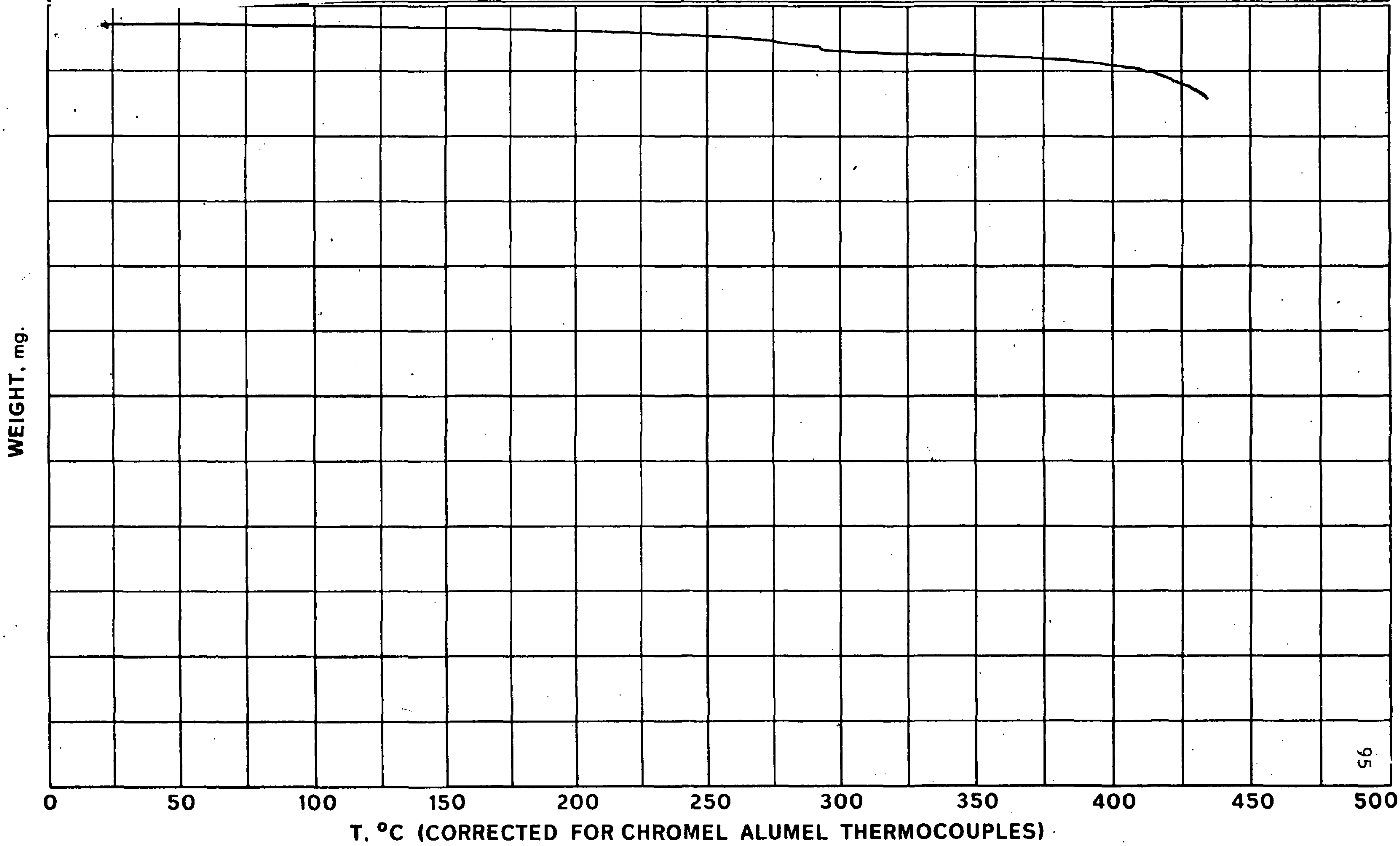
DUPONT INSTRUMENTS

SAMPLE: Figure 41 Panel No. 8 11.6 mg (No suppression)	**X-AXIS** TEMP. SCALE 50 °C/inch SHIFT 0 inch	**Y-AXIS** SCALE 2 mg./inch (SCALE SETTING X 2) SUPPRESSION 0 mg.	RUN NO. ____ DATE 12/15/72 OPERATOR HK HEATING RATE 15 °C/min. ATM. AIR TIME CONSTANT 5 sec.



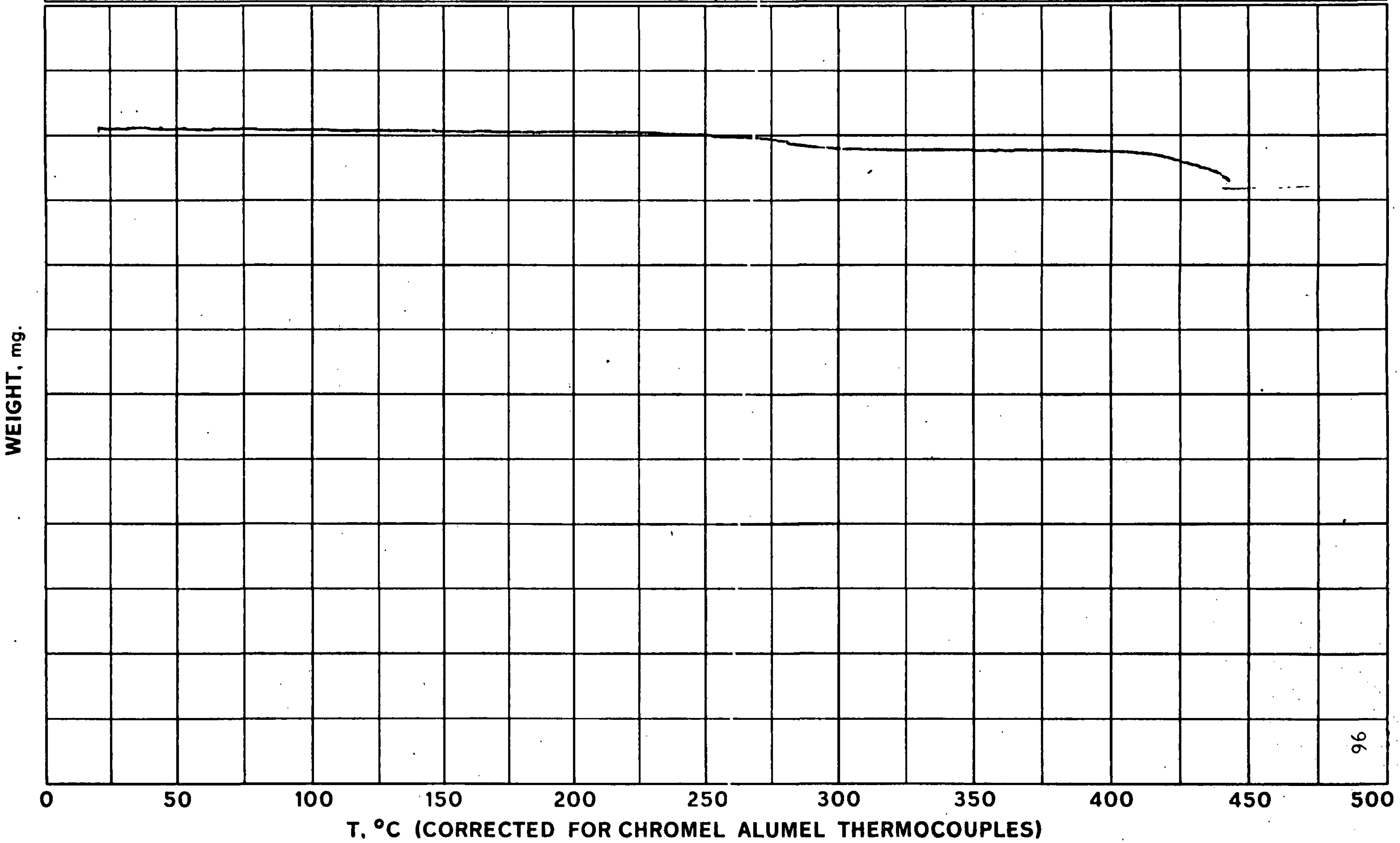
DU PONT INSTRUMENTS

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. ______ DATE 12/21/71
Figure No. 42	TEMP. SCALE 50 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR HK
Panel No. 9	SHIFT 0 inch		HEATING RATE 15 °C/min.
11.7 mg (No suppression)		SUPPRESSION 0 mg.	ATM. AIR
			TIME CONSTANT 5 sec.



DU PONT INSTRUMENTS

SAMPLE:	**X-AXIS**	**Y-AXIS**	**RUN NO.** DATE 11/4/72
Figure No. 43	TEMP. SCALE 50 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR ECF
Panel No. 10	SHIFT 0 inch		HEATING RATE 10 °C/min.
10.1 mg (No suppression)		SUPPRESSION 0 mg.	ATM. air
			TIME CONSTANT 2 sec.



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