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UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA 46556

PROGRESS REPORT NUMBER 7

ON THE

FUNDAMENTAL STUDIES ON THE SYNTHESIS OF HEAT-RESISTANT POLYMERS

THE SYNTHESIS AND EVALUATION OF POLYMERIC SCHIFF BASES FROM XYLYLIDENE TETRAALKYL ETHERS

PERFORMED

UNDER

NASA GRANT NsG339

BY

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NOTRE DAME, INDIANA 46556

SEPTEMBER 15, 1965

FOREWORD

This report is a summary report of the researches performed under NASA Grant NsG339 for the period 31 January 1965 to 15 September 1965 on the synthesis of heat-resistant polymers. The technical aspect of this grant is administered by Mr. Bernard Achhammer, Office of Advanced Research and Technology, NASA Headquarters, Washington, D.C. 20546.

The research under this grant is being conducted in the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556 under the technical direction of Professor G. F. D'Alelio, principal investigator.

This report covers studies performed by G. F. D'Alelio and Thomas Ostdick, O.S.B.

Date September 15, 1965

Signed G. F. D'Alelio

G. F. D'Alelio
Principal Investigator

ABSTRACT

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Black polymeric Schiff bases, which pass through a fusible stage, have been synthesized, from p-xylylidenetetra-n-butyl ether and either m- or p-phenylenediamine or their benzylidene derivatives in the absence or presence of benzalaniline as a solvent. The differences between the polymers are small. The polymers derived from m-phenylenediamine and its benzylidene derivative have heat-resistance properties at least as high as those prepared from the para compounds and are equivalent to Schiff base polymers prepared by bis-Schiff base exchange reactions. The syntheses from the meta compounds proceed more smoothly than the para compounds. Since the cost of m-phenylenediamine is much lower than the p-phenylenediamine, the use of the meta diamine is preferred and recommended. When the condensation of the reagents is carried to a temperature in the range of 425°C to 600°C, the heat-resistance of the best polymers is 550°C in air (1022°F), and 675°C (1247°F) in nitrogen. When the condensation is carried to a temperature of 1176°C, the best polymers show a heat-resistance of 600°C (1112°F) in air and 1176°C (2026°F) in nitrogen. Some secondary reaction appears to occur when the polymers are heated at above 600°C in nitrogen and the resulting polymers are not typical chars but retain their bright, shiny appearance.

Author

TABLE OF CONTENTS

I. Introduction.

In a previous report,[1] a number of reaction systems for the synthesis of conjugated polymeric Schiff bases were proposed for further study. Such studies were necessary to assist in the final selections of the polymerization systems which produce polymers with the best properties of heat resistance.

This report concerns investigations of the synthesis and heat-resistance properties of polymers arising from the reaction of xylylidenetetra-n-alkyl ethers with meta- and para-phenylenediamines and their dibenzylidene derivatives, as well as of the influence of benzalaniline as solvent and of the effects of postheating on the heat-resistant properties of the polymers.

Earlier work[1] had used xylylidenetetraethyl ether and xylylidenetetra-n-butyl ether as the aldehyde derivatives in the syntheses of the polymeric Schiff bases. In the present work the butyl derivative is used exclusively. It appears to be an ideal reagent for these reactions because it is easily prepared and also because its reactivity, which is lower than that of the ethyl derivative, allows a longer reaction time during the fusible polymer stage in the polymerization process.

The polymerization reactions investigated in these studies are given by the following equations:

$$\mathrm{n\ (H_9C_4O)_2CHC_6H_4CH(OC_4H_9)_2 + n\ H_2NC_6H_4NH_2 \longrightarrow}$$

$$\mathrm{4n\ C_4H_9OH + \left[HCC_6H_4CH{=}NC_6H_4N\right]_n} \qquad \text{(eq. 1)}$$

and

$$\mathrm{n\ (H_9C_4O)_2HCC_6H_4CH(OC_4H_9)_2 + n\ C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5 \longrightarrow}$$

$$\mathrm{2n\ C_6H_5CHO(C_4H_9)_2 + \left[HCC_6H_4CH{=}NC_6H_4N\right]_n} \qquad \text{(eq. 2)}$$

It was indicated in a previous report, that m-phenylenediamine and its dibenzylidene derivative appeared to be better reactants than the analogous para compounds since the meta compounds permitted a longer fusible stage during the polymer syntheses. For this reason both the meta and the para phenylenediamines were evaluated individually and as mixtures. Also, the meta and the para dibenzylidenephenylenediamines were reacted individually to contrast their behaviors.

The polymerization reactions between the acetal and the free amines were performed without the addition of catalysts, whereas, because of the low rate of reaction between the acetal and the dibenzylidenephenylenediamines, small amounts of zinc chloride were used as the Lewis acid catalyst. The amount of zinc chloride used was arbitrarily chosen on the basis of previous studies[1] and does not necessarily represent the ideal quantity. Benzalaniline was used in a number of the reactions studied to determine whether or not it facilitated the formation of black polymers while producing higher-than-theoretical yields.

Some of the objectives of these studies were to produce black polymers which pass through a fusible stage from the reactions investigated and to evaluate their thermal properties and to contrast them with the thermal properties of the yellow polymers, even though the yellow polymers are of the infusible, brick-dust type.[2]

It was also necessary in these exploratory studies to select arbitrarily the reaction conditions for the polymerization. Previous studies[3] have shown that the polycondensation reaction involving exchange reactions in the synthesis of polymeric Schiff bases is far from complete, unless the temperature of condensation exceeds 400°C; in fact, it is not truly completed until the temperature of condensation exceeds 600°C. This[3] was evidenced by the continued elimination of benzalaniline when the polymeric

Schiff bases synthesized by the Bis-Schiff base exchange reactions were heated up to 1200°C in nitrogen in a thermogravimetric apparatus; these same preheated polymers, when reheated to 1200°C in nitrogen, showed minor weight losses.

For the studies in this report, it was decided to prepare all the polymers under the identical temperature conditions of condensation up to 320°C under an arbitrary time and pressure schedule which would be maintained uniformly for all the polymerizations whenever feasible. The polymers prepared up to a condensation temperature of 320°C would then be isolated and divided into portions to be postheated to 425°C and 600°C. A temperature of 650-700°C would have been preferable to 600°C as the selected second highest temperature for postheating but this was unfeasible because these temperatures are beyond the melting point of the aluminum block (623°C) used as the metal-heating apparatus and the operating conditions of the heating mantle surrounding the aluminum block.

It was considered advisable also to complete the condensation at temperatures in excess of 600°C and preferably to the region of 1000°C or higher. This was accomplished by heating small samples of the order of 10 mg. of the polymer directly in the thermogravimetric apparatus.

It was realized that in utilizing an arbitrarily chosen schedule of temperature, time, and pressure that the ultimate yields would not necessarily be the highest or the best attainable, since, if the polycondensation is not complete when the pressure over the condensation mass is reduced, reagents and oligomer may be lost reducing ultimate yields. However, in condensations which proceed by elimination of simple molecules by chain-end coupling, the ultimate polymer obtained, even at reduced yields, can be considered as sufficiently typical for evaluation of thermal properties, if condensation reaction is continued far enough.

It is also a purpose of this study to evaluate the thermal properties of the polymers by thermogravimetric methods in atmospheres of nitrogen and air.

II. Polymerization Reactions.

A. General Experimental Technique.

In all of the polymerization reactions included in this study, the same experimental set-up was used. Reactants were combined in a 50 ml. round-bottomed reaction flask. The reaction flask was then equipped with a thermometer supported by a Teflon adapter and with a simple distilling heat fitted with a thermometer, a condenser, an adapter, and a receiver. All joints were ground glass and standard taper. The reaction flask was heated by means of an electric mantle; the receiver was submerged in a solid carbon dioxide-acetone trap. The adapter had a side arm to facilitate attachment to a vacuum line during part of the reaction.

The monomers used in these reactions were prepared by the procedures given in a previous report.[1]

With several exceptions as indicated below, the following reaction schedule was used for all polymerizations:

1.5 hours at 100-130°C at atmospheric pressure
1.0 hours at 130-150°C at atmospheric pressure
17.0 hours at 150-230°C at atmospheric pressure
23.0 hours at 230-320°C under reduced pressure in the range of 0.6 to 1.2 mm Hg.

B. Individual Reactions of Xylylidenetetra-n-butyl Ether (XTBE) with Phenylenediamines (PDA) and Their Derivatives.

1. Experimental.

a. With the Phenylenediamines (PDA).

i. Reactions of Xylylidenetetra-n-butyl Ether (XTBE) with m-Phenylenediamine (MPDA).

a) (DA-37-12) in Benzalaniline (BA).

A mixture of 4.512 g. (0.0139 M) of xylylidenetetra-n-butyl ether (XTBE), 1.495 g. (0.0144 M) m-phenylenediamine (MPDA), and 5.019 g. benzalaniline (BA) was reacted. Conditions of raction and results are given in Table 1. The yield of black fused polymer, which was medium brown after being ground, was 4.75 g. (166% yield).

b) (DA-37-13) Without BA.

A mixture of 4.425 g. (0.0137 M) of XTBE and 1.410 g. (0.0136 M) of MPDA were reacted. The observations are given in Table 1. The yield of black fused polymer, which was dark-brown after being ground, was 2.33 g. (106% yield).

ii. Reaction of XTBE with Mixture of m- and p-Phenylenediamine (PDA).

a) (DA-37-17) 75 Mole % of MPDA.

A mixture of 3.2223 g. (0.0081 M) of XTBE, 0.631 g. (0.0061 M) of MPDA and 0.2106 g. (0.0020 M) of p-phenylenediamine (PPDA) was reacted. The observations are given in Table 1. The yield of brown fused polymer, which was brown after being ground, was 1.70 g. (102% yield).

b) (DA-37-14) 50 Mole % of MPDA.

A mixture of 5.5321 g. (0.00140 M) of XTBE, 0.7265 g. (0.0070 M) of MPDA and 0.7266 g. (0.0070 M) of PPDA was reacted. The observations are given in Table 1. The yield of black fused polymer, which was brown after being ground, was 2.97 g. (103% yield).

c) (DA-37-18) 25 Mole % of MPDA.

A mixture of 3.2743 g. (0.0083 M) of XTBE, 0.2158 g. (0.0021 M) of MPDA and 0.6474 g. (0.0061 M) of PPDA was reacted. The observations are given in Table 1. The yield of brown-black partially fused polymer, which

Table 1

Observations During Reactions of XTBE with PDA and Derivatives Under Standardized Conditions

	1.5 hours at 100-130°C/ atm. press.	1.0 hour at 130-150°C/ atm. press.	17.0 hours at 150-230°C/ atm. press.	23.0 hours at 230-320°C/mm Hg		Yield % of Theory
DA-37-12						
Appearance	orange liquid	red-brown liquid	black solid; some liq.	black solid	1.2	166
Distillate	none	3.61 g. (88%) n-BuOH	none	1.93 g.		
DA-37-13						
Appearance	two layers	red-brown liq. & solid	black solid; some liq.	black solid	1.2	106
Distillate	none	360 g. (89%) n-BuOH	none	0.32 g.		
DA-37-14						
Appearance	two layers	red-brown liq. & solid	orange solid	black solid	0.3	103
Distillate	none	3.62 g. (88%) n-BuOH some sublimation	none	none		
DA-37-15						
Appearance	yellow paste	yellow liquid; some sublimed solid	dark yellow liquid	brown solid	0.8	145
Distillate	none	2.24 g. (90%) n-BuOH	none	3.37 g.		
DA-37-16						
Appearance	red-brown liquid	some sublimed solid	yellow-brown solid	brown-black solid	0.8	103
Distillate	none	2.14 g. (85%) n-BuOH	none	0.25 g.		
DA-37-17						
Appearance	two layers	yellow-brown soft melt	brown solid	brown solid	0.6	102
Distillate	none	2.34 g. (99%) n-BuOH	none	0.43 g.		
DA-37-18						
Appearance	two layers	brown liq.; some sublimed solid	brown solid	brown-black solid	0.7	101
Distillate	none	2.20 g. (90%) n-BuOH	none	none		
DA-37-20						
Appearance	tan liq., some solid	little solid left	black solid & liquid	black solid	0.6	125
Distillate	none	none	1.30 g., yellow liq.	1.5 g. dark, acetone soluble liq.		
DA-37-22						
Appearance	yellow-brown liq.	no solid	black solid & liq.	black solid	0.8	171
Distillate	none	none	1.14 g. yellow liq.	negligible		

was chocolate-brown after being ground, was 1.73 g. (101% yield).

iii. Reactions of XTBE with p-Phenylenediamine (PPDA).

a) (DA-37-15) In BA.

A mixture of 3.3079 g. (0.0084 M) of XTBE, 0.8736 g. (0.0084 M) of PPDA and 5.3649 g. of BA was reacted. The observations are given in Table 1. The yield of brown unfused polymer, which was orange-brown after being ground, was 2.51 g. (145% yield).

b) (DA-37-16) Without BA.

A mixture of 3.3606 g. (0.0083 M) of XTBE and 0.8840 g. (0.0085 M) of PPDA was reacted. The observations are given in Table 1. The yield of brown-black partially fused polymer, which was brown after being ground, was 1.80 g. (103% yield).

1) (DA-37-19) With Initial Reflux.

A mixture of 3.3584 g. (0.0085 M) of XTBE and 0.8840 g. (0.0085 M) of PPDA was reacted under the following conditions:

Conditions	Hours	Observations
reflux 120°C/atm.press.	16	yellow solid
130-150°C/atm.press.	1	yellow solid 2.19 g. (87%) n-BuOH
150-230°C/atm. press.	17	dark yellow solid
230-320°C/0.6 mm Hg	23	black solid

The yield of black unfused polymer, which was yellow-brown after being ground, was 1.77 g. (101% yield); Table 2.

2) (DA-37-24) To Obtain Yellow Polymer.

A mixture of 0.6721 g. (0.0017 M) of XTBE and 0.1768 g. (0.0017 M) of PPDA was reacted under the following conditions:

Conditions	Hours	Observations
100-130°C/atm.press.	1.5	two layers
130-150°C/atm.press.	1.0	some solid sublimation
150-320°C/0.6 mm Hg	0.5	dark yellow solid

The yield of dull, unfused yellow polymer was 0.385 g. (110% yield); Table 2.

b. With Dibenzylidenephenylenediamines.

i. Reactions of XTBE with Dibenzylidene-m-phenylenediamine (DBMPD).

a) (DA-37-23) In BA.

A mixture of 2.8166 g. (0.0071 M) of XTBE, 2.0077 g. (0.0071 M) DBMPD, 4.6 g. of BA, and 0.1 g. of $ZnCl_2$ was reacted under the following conditions:

Conditions	Hours	
100-130°C/atm. press.	1.5	brown liq.; some solid reactant left
130-150°C/atm. press.	1.0	no solid left
150-230°C/atm. press.	17.0	black opaque liq., 1.39 g. yellow distillate
230-320°C/0.8 mm Hg	47.0	23 hrs., black liq. 47 hrs., black solid 3.8 g. brown, acetone-soluble distillate

The yield of black, shiny polymer, which was brown-black after being ground, was 3.25 g. (223% yield); Table 2.

b) (DA-37-22) Without BA.

A mixture of 2.8116 g. (0.0071 M) of XTBE, 2.0165 g. (0.0071 M) of DBMPD, and 0.1 g. of $ZnCl_2$ was reacted. The observations are given in Table 1. The yield of black, shiny polymer, which was brown-black after being ground, was 2.50 g. (171% yield).

ii. Reactions of XTBE with Dibenzylidene-p-phenylenediamine (DBPPD).

a) (DA-37-21) In BA.

A mixture of 3.3617 g. (0.0085 M) of XTBE, 2.4140 g. (0.0085 M) of DBPPD, 5.2493 g. of BA, and 0.01 g. of $ZnCl_2$ was reacted under the following conditions:

Conditions	Hours	Observations
100-130°C/atm. press.	1.5	brown liquid; some solid reactant left
130-150°C/atm. press.	1.0	no solid left; all liquid
150-230°C/atm. press.	17.0	black opaque liquid, 0.99 g. yellow distillate
230-320°C/0.8 mm Hg	47.0	23 hrs., black liquid 47 hrs., black solid 6.0 g. brown, acetone-soluble distillate

The yield of black, shiny polymer, which was brown after being ground, was 3.13 g. (179% yield); Table 2.

b) (DA-37-20) Without BA.

A mixture of 3.0807 g. (0.0078 M) of XTBE, 2.2152 g. (0.0078 M) of DBPPD, and 0.09 g. of $ZnCl_2$ was reacted. The observations are given in Table 1. The yield of black, shiny polymer, which was brown after being ground, was 2.02 g. (125% yield).

Table 2

Observations During Reactions of XTBE
With PDA and Derivatives Under Varied Conditions

Experiment Number	Color of Polymer	Yield, % of Theory
DA-37-19	black, unfused	101
DA-37-21	black, shiny	179
DA-37-23	black, shiny	223
DA-37-24	yellow, brick dust	110

2. General Discussion.

The purpose of these reactions was to obtain polymers which, through thermogravimetric studies, would reveal the influence of varying the starting materials and reaction conditions on the heat resistance of the polymers. These studies were undertaken to provide a means for distinguishing between the advisability of starting with the free m-diamine or p-diamine, or their corresponding benzylidene derivatives, and whether or not a solvent is required to prepare satisfactory polymers in these reactions.

Earlier work[1] showed that benzalaniline is the most active medium in which to perform this class of polymerizations. Hence this compound was chosen for use as a solvent in the studies. It appears to function not only as a solvent but also as a reagent.[1,2] The comparison in behavior between the four reagents, namely, the meta and the para phenylenediamines and their corresponding dibenzylidene derivatives was motivated by economic factors. First, the dibenzylidene derivatives require synthesis from the free amine by means of benzaldehyde thereby increasing their cost over the free amine. Secondly, the m-phenylenediamine is relatively inexpensive since it can be prepared easily from low-cost m-dinitrobenzene by catalytic hydrogenation. In contrast, p-phenylenediamine involves more steps in its synthesis and accordingly is higher in cost.

It was observed in these studies that in the absence of solvent m-phenylenediamine (DA-37-13) reacted with xylylidenetetra-n-butyl ether more smoothly, producing homogeneous liquid melts and intermediate fusible polymers for longer periods of time, than the p-phenylenediamine (DA-37-16). The p-phenylenediamine reacted more rapidly than its meta analogue causing earlier precipitation of lower molecular weight polymers with the result that sublimation of reactants occurred later in the process. In fact, in every other case where p-phenylenediamine was used in admixtures with m-phenylenediamine, (DA-37-14, DA-37-17 and DA-37-18), sublimation of reactants to the upper part of the flask occurred early in the reaction. The presence of p-phenylenediamine in admixtures with m-phenylenediamine in the range of 75-25 to 25-75 mole per cent also cause premature precipitation of polymer which appeared as a solid dispersed in the liquid which persisted for many hours in the reaction. It was also evident in these reactions that the by-products were more readily removed in the reactions using m-phenylenediamine than in those in which p-phenylenediamine was a reactant.

The exchange reactions of xylylidenetetra-n-butyl ether with the dibenzylidenephenylenediamines are much slower than the free amines and necessitate the use of a catalyst. The difference in behavior between the m-dibenzylidenephenylenediamine (DA-37-22) and the p-dibenzylidenephenylenediamine (DA-37-20) was not as marked as it was between their parent diamines. However, there were notable differences between the two compounds in that with the meta derivative the viscous melt persisted for a longer period of time, and that the by-product elimination was more complete as evidenced by the yield of 125% for the meta and 171% for the para derivatives. In terms of overall behavior during polymer syntheses the meta derivative is preferred over the para derivative.

Since at 320°C, the condensation polymerization is <u>far</u> from complete, the yields of polymers, compared to 100% theoretical yield calculation on a $\overline{DP}_n$ of ∞, are obviously not ultimate yields and all of them should be greater than 100%, especially in the cases where benzalaniline is used as a solvent. In every case where BA was used as a solvent, (DA-37-12, DA-37-15, DA-37-21 and DA-37-23), the yield was much higher than theoretical, confirming previous studies[1-3] that this compound is a coreactant as well as a solvent.

In the reaction of XTBE with the free amines, (DA-37-13, DA-37-14, DA-37-16, DA-37-17, and DA-37-18), the yields obtained by condensation up to 320°C were in the vicinity of 100% of theory varying from 101% to 106%; these values should be higher, of the order of 110% or higher. The low yields at this stage of the reaction is attributed to incomplete reaction and loss of XTBE under reduced pressure. Low values of this kind were also obtained when the reagents were refluxed (DA-37-19) and when the deliberate synthesis of a yellow polymer (DA-37-24) was achieved. For the present purpose these low yields are not of consequence; whereas for the future there is indicated an area of studies involving the evaluation of other lower alkyl ethers of terephthaldehyde and of Lewis acid catalysts, such as zinc chloride.

III. Postheating of Polymers.

The polymers prepared in this report were condensed to a temperature of 320°C; a temperature at which the polycondensation is incomplete. The polymers thus prepared were then divided into appropriate portions and postheated to temperatures higher than 320°C to increase their molecular weights.

A. Postheating at 425°C and 600°C.

Since a number of polymerizations in the previous reports[1-3] were terminated at a reaction temperature in the range of 400°C to 425°C, a portion of the polymer prepared at 320°C was postheated to approximately 425°C.

In other studies,[3] it was shown that condensation continued to temperatures in the 600°C range with by-product elimination and without substantial changes in the infrared spectra of the polymer. Accordingly, in these studies another portion of the polymer prepared at 320°C was postheated to 600°C. The designation H425 or H600 is placed at the end of the number of a polymer to indicate that the polymer has been heated at 425°C or at 600°C respectively. For example, DA-37-12-H425 is polymer DA-37-12 after it has been postheated at 425°C.

1. General Experimental Technique.

Polymers were placed in a quartz tube fitted with a side arm and heated by means of a metal heat sink which consisted of a cube of aluminum, three-inches long on an edge. A hole, one inch in diameter, was drilled in the center of one face of the cube to house the quartz tube, and a probe hole was located within one-half inch of the inserted quartz tube. The metal cube was heated by a quartz mantle, custom-made for the cube.

For the 425°C postheating, the temperature was maintained and controlled by a Model 1422-071 Temperature Controller from Cole-Parmer Instrument and Equipment Company. For the 600°C postheating, the temperature was controlled by a Variac and the temperature determined by a thermocouple.

The sample was placed in a reaction tube equipped with a nitrogen bleeder supported by a Teflon adapter, a condenser, an adapter with side arm for evacuation, and a receiver which was submerged in a solid carbon dioxide-acetone trap. All joints were ground glass and standard taper.

Samples were weighed into the reaction tube, the other glassware was attached, and the tube placed into the aluminum cube, which had already reached the desired temperature. The system was evacuated and nitrogen was bled in. After a few minutes in the post heating at 425°C the nitrogen bleeder was sealed off, while in the 600°C postheating the flow of nitrogen was continued through the heating period.

For all of the postheating at 425°C the tubes were left in the aluminum block for forty hours. In the case of the 600°C postheating, the tubes were left in the heating block for twenty minutes.

B. Postheating of Individual Polymers.

1. Experimental.

Table 3 lists the experimental data for the postheating of the polymers. Table 4 provides a summary of the percentage yields of the polymers before and after postheating. The percentages were calculated by projecting the weight loss over the original yield. In the case of postheating of four of the polymers at 600°C, when the tube containing the original polymer was placed in the heating block, some finely ground polymeric material rose to the top of the reaction tube and this also became black during the course of the postheating. The gram yields given in Table 3 and the percentage yields in Table 4 refer to the total amount of material in the bottom and in the top of the reaction tube for these four polymers. Values for the separate parts of these polymers follows:

Polymer	Weight of Material Found	
	in bottom of tube	in top of tube
DA-37-12-H600	0.7188 g.	0.1870 g.
DA-37-13-H600	0.2130 g.	0.1954 g.
DA-37-14-H600	0.3652 g.	0.0418 g.
DA-37-17-H600	0.2655 g.	0.1918 g.

Table 3

Data for Postheating

Original Polymer	Weight of Polymer Used, g.	Gram Yield of H425 Polymer	Appearance of H425 Polymer	Weight of Polymer Used, g.	Gram Yield of H600 Polymer	Appearance of H600 Polymer
DA-37-12	1.4277	1.1547	black, slightly shiny powder	1.3550	0.9058	in bottom: black, steel-like solid in top: black, dull powder
DA-37-13	0.6037	0.5866	black, shiny powder	0.5473	0.4084	in bottom: black, steel-like solid in top: black, dull powder
DA-37-14	0.6663	0.5267	black, dull powder	0.6201	0.4070	in bottom: black, shiny powder in top: black, dull powder
DA-37-15	0.5754	0.3393	black, dull powder	0.9188	0.4251	black, dull pellet
DA-37-16	0.5311	0.3790	black, dull powder	0.5517	0.2975	black, dull powder
DA-37-17	0.5174	0.4379	black, shiny powder	0.6258	0.4573	in bottom: black, steel-like solid in top: black, dull powder
DA-37-18	0.5158	0.3875	black, dull powder	0.6088	0.3092	black, dull powder
DA-37-19	0.4699	0.3452	black, dull powder	0.6408	0.3536	brown-black, dull powder
DA-37-20	0.7714	0.3028	black, dull pellet			
DA-37-21	0.5745	0.2861	black, dull pellet			
DA-37-22	0.5837	0.5006	black, dull pellet			
DA-37-23	0.5370	0.2181	black, steel-like solid			

Table 4

Summary of Percentage Yields of Polymers

Original Polymer	% Yield of original polymer	% Yield after heating at 425°C	% Yield after heating at 600°C
DA-37-12	166	134.0	111
DA-37-13	106	103.0	79
DA-37-14	103	81.5	67
DA-37-15	145	85.5	67
DA-37-16	103	73.5	55
DA-37-17	103	86.3	74
DA-37-18	101	75.8	51
DA-37-19	101	74.2	56
DA-37-20	125	49.1	---
DA-37-21	179	89.0	---
DA-37-22	171	146.6	---
DA-37-23	223	90.6	---

C. Postheating at Temperatures Above 600°C.

It is desirable to evaluate the thermal and other properties of polymers which have been heated to temperatures above 600°C, preferably to temperatures in the vicinity of 1000°C, and means for achieving this heat treatment had to be devised. The apparatus used in heat-treating the polymers to 425°C and 600°C is not suitable for this purpose since the temperature limitation on the heating mantle is set at about 610°C. Accordingly, the du Pont 950 Thermogravimetric Analyzer was adopted for this purpose in the following manner. The sample was placed in the TGA cell of the 950 Analyzer and heated, under nitrogen, to a recorded 1200°C, which is corrected for the non-linearity of the chromel-alumel thermocouples to 1176°C. Then the furnace and the sample was allowed to cool to room temperature in nitrogen. These samples are designated by the addition of R to the polymer number and are designated as recycles.

D. General Discussion.

A discussion of the effect of postheating on the thermal stability of the polymers is left to the section on thermogravimetric analyses.

Nothing was found in the solid carbon dioxide-acetone trap after any of the postheatings at 425°C, although it is possible that some highly volatile material may have gone through the trap. However, in every case a yellow-brown deposit formed on the upper part of the reaction tube. The yellow-brown deposit is probably due to solvent (benzalaniline) in the cases where solvent was present as well as to the elimination of telogens from the ends of chains with resultant chain lengthening.

IV. Thermogravimetric Analyses.

The du Pont 950 Thermogravimetric Analyzer was used to determine the thermal properties of the polymers under conditions identical to those used in other studies.[3] The heating rate used was 15°C per minute. A number of thermogravimetric measurements were made in nitrogen and in air at a flow rate of one (1) standard liter per minute. Sample weight was standarized at 10 mg. A temperature correction has been made in the measurements for the mon-linearity of the chromel-alumel thermocouples.

A. Experimental.

1. Thermoanalysis in Air.

The polymers listed in Table 5 were subjected to thermogravimetric analysis in air and the thermograms obtained for the respective polymers are given under the appendix number. The data in Table 6 gives the percentage of loss of weight at 400°C, 500°C, 600°C and 700°C in air under the conditions of measurement. The data in Table 7 lists the temperature for each polymer at which weight loss beging, the temperature at which 20% of the weight has been lost, and the temperature at which the sample had completely combusted in air to zero weight.

Table 5

Polymers Thermoanalyzed in Air

Thermogram Appendix Number	Polymer Number	Thermogram Appendix Number	Polymer Number
1	DA-37-12	18	DA-37-17-H600
2	DA-37-12-H425	19	DA-37-18
3	DA-37-12-H600	20	DA-37-18-H425
4	DA-37-13	21	DA-37-18-H600
5	DA-37-13-H425	22	DA-37-19
6	DA-37-13-H600	23	DA-37-19-H425
7	DA-37-14	24	DA-37-19-H600
8	DA-37-14-H425	25	DA-37-20
9	DA-37-14-H600	26	DA-37-20-H425
10	DA-37-15	27	DA-37-21
11	DA-37-15-H425	28	DA-37-21-H425
12	DA-37-15-H600	29	DA-37-22
13	DA-37-16	30	DA-37-22-H425
14	DA-37-16-H425	31	DA-37-23
15	DA-37-16-H600	32	DA-37-23-H425
16	DA-37-17	33	DA-37-24
17	DA-37-17-H425		

Table 6

Percentage Loss of Weight of Polymers at
Various Temperatures While Being Heated in Air

Thermogram Appendix Number	Polymer	% Loss at 400°C	% Loss at 500°C	% Loss at 600°C	% Loss at 700°C
1	DA-37-12	2.5	20	86	100
2	DA-37-12-H425	0	1	32	94
3	DA-37-12-H600	0	1	28	97
4	DA-37-13	4	38	88	100
5	DA-37-13-H425	0	1	39	99
6	DA-37-13-H600	0	1	21	97
7	DA-37-14	1	25	89	100
8	DA-37-14-H425	0	1	42	94
9	DA-37-14-H600	0	8	80	96
10	DA-37-15	20	29	73	100
11	DA-37-15-H425	0	2	48	99
12	DA-37-15-H600	0	27	97	100
13	DA-37-16	7	73	100	100
14	DA-37-16-H425	0	2	78	100
15	DA-37-16-H600	0	52	93	100
16	DA-37-17	1	18	62	100
17	DA-37-17-H425	0	12	52	97
18	DA-37-17-H600	0	6	88	100
19	DA-37-18	4	31	92	100
20	DA-37-18-H425	0	1	22	100
21	DA-37-18-H600	0	18	100	100
22	DA-37-19	0	67	95	100
23	DA-37-19-H425	0	1	80	100
24	DA-37-19-H600	0	77	93	100
25	DA-37-20	5	56	90	100
26	DA-37-20-H425	0	16	68	100
27	DA-37-21	3	48	91	100
28	DA-37-21-H425	2	43	97	100
29	DA-37-22	4	35	83	100
30	DA-37-22-H425	0	54	93	100
31	DA-37-23	0	9	68	100
32	DA-37-23-H425	0	11	38	97
33	DA-37-24	4	60	81	100

Table 7

Temperatures at Which Weight Loss Begins, Has Occurred to 20%, is Complete While Being Heated in Air

Polymer	Sample Begins to Lose Weight at °C	Sample Has Lost 20% at °C	Sample Has Disappeared at °C
DA-37-12	320	500	670
DA-37-12-H425	470	583	790
DA-37-12-H600	460	593	725
DA-37-13	350	477	650
DA-37-13-H425	450	575	740
DA-37-13-H600	480	595	742
DA-37-14	370	490	670
DA-37-14-H425	430	580	775
DA-37-14-H600	440	517	800
DA-37-15	105	390	670
DA-37-15-H425	440	580	720
DA-37-15-H600	400	498	640
DA-37-16	200	450	600
DA-37-16-H425	480	552	690
DA-37-16-H600	400	480	640
DA-37-17	380	502	710
DA-37-17-H425	395	520	735
DA-37-17-H600	400	515	670
DA-37-18	340	490	660
DA-37-18-H425	515	595	688
DA-37-18-H600	410	500	585
DA-37-19	396	400	720
DA-37-19-H425	485	535	660
DA-37-19-H600	390	455	670
DA-37-20	340	463	650
DA-37-20-H425	370	497	660
DA-37-21	355	482	640
DA-37-21-H425	350	482	630
DA-37-22	350	470	710
DA-37-22-H425	380	460	630
DA-37-23	420	503	700
DA-37-23-H425	400	550	921
DA-37-24	150	455	680

2. Thermoanalyses in Nitrogen and Recycles in Nitrogen and Air.

a. In Nitrogen.

The thermograms of a number of polymers as prepared at 320°C, or post-heated at 425°C or 600°C were also obtained under a nitrogen atmosphere. The nitrogen used was lamp-grade nitrogen obtained from General Electric Company and used without further purification. Table 8 lists, in the second column, the polymers which, as prepared, were heated in nitrogen, and the appendix numbers of the thermograms in which curve number 1 plots the data obtained under nitrogen to a temperature of 1176°C. Table 9 gives the percentage loss of weight at 400°C, 600°C, 800°C, 1000°C, and 1176°C during this first heating in nitrogen.

b. Recycle in Nitrogen.

The polymers heated in nitrogen to 1176°C were considered as fully condensed and as being heat-treated to temperatures in excess of 600°C. Accordingly the polymer samples, after heating to 1176°C, were recycled to 1176°C in nitrogen. The polymers so treated are listed in column 3 in Table 8 with the appendix designation R to indicate recycle together with the appendix number of the termograms in which curve 2 plots the data obtained. Table 10 lists the percentage loss in weight of the polymers on recycled heating to 1176°C based on the amount of polymer left after the first heating to 1176°C, and on weight of the original sample.

Table 8

Polymers Thermoanalyzed in Nitrogen, Then Recycled in Nitrogen, Followed by Recycle in Air

Thermogram Appendix Number	Run in Nitrogen, Curve No. 1	Recycled in Nitrogen, Curve No. 2	Recycled in Air Curve No. 3
34	DA-37-12	DA-37-12-R	DA-37-12-R-a
35	DA-37-12-H425	DA-37-12-H425-R	DA-37-12-H425-R-a
36	DA-37-12-H600	DA-37-12-H600-R	DA-37-12-H600-R-a
37	DA-37-13	DA-37-13-R	DA-37-13-R-a
38	DA-37-13-H425	DA-37-13-H425-R	DA-37-13-H425-R-a
39	DA-37-13-H600	DA-37-13-H600-R	DA-37-13-H600-R-a
40	DA-37-14-H600	DA-37-14-H600-R	DA-37-14-H600-R-a
41	DA-37-15	DA-37-15-R	DA-37-15-R-a
42	DA-37-15-H425	DA-37-15-H425-R	DA-37-15-H425-R-a
43	DA-37-15-H600	DA-37-15-H600-R	DA-37-15-H600-R-a
44	DA-37-16	DA-37-16-R	DA-37-16-R-a
45	DA-37-16-H425	DA-37-16-H425-R	DA-37-16-H425-R-a
46	DA-37-16-H600	DA-37-16-H600-R	DA-37-16-H600-R-a
47	DA-37-17-H600	DA-37-17-H600-R	DA-37-17-H600-R-a
48	DA-37-18-H600	DA-37-18-H600-R	DA-37-18-H600-R-a
49	DA-37-19-H600	DA-37-19-H600-R	DA-37-19-H600-R-a
50	DA-37-20-H425	DA-37-20-H425-R	DA-37-20-H425-R-a
51	DA-37-21	DA-37-21-R	DA-37-21-R-a
52	DA-37-22-H425	DA-37-22-H425-R	DA-37-22-H425-R-a
53	DA-37-23-H425	DA-37-23-H425-R	DA-37-23-H425-R-a
54	DA-37-24	DA-37-24-R	DA-37-24-R-a

Table 9

Percentage Loss of Weight of Selected Polymers at Various Temperatures While Being Heated in Nitrogen

Thermogram Appendix Number	Polymer	% Loss at 400°C	% Loss at 600°C	% Loss at 800°C	% Loss at 1000°C	% Loss at 1176°C
34	DA-37-12	0.0	21.0	27.0	30.0	36.0
35	DA-37-12-H425	0.0	3.0	10.5	15.0	22.0
36	DA-37-12-H600	0.0	3.0	9.5	12.0	17.0
37	DA-37-13	1.0	20.0	27.0	30.0	35.0
38	DA-37-13-H425	0.0	2.0	12.0	16.0	22.0
39	DA-37-13-H600	0.0	2.0	7.5	11.0	16.0
40	DA-37-14-H600	0.0	1.0	6.0	10.0	15.0
41	DA-37-15	14.0	43.0	52.0	53.0	56.0
42	DA-37-15-H425	0.0	6.0	18.0	21.0	22.5
43	DA-37-15-H600	0.0	1.0	7.5	11.0	15.0
44	DA-37-16	3.0	39.0	51.0	54.0	56.5
45	DA-37-16-H425	0.0	2.0	18.0	23.0	27.0
46	DA-37-16-H600	0.0	1.0	10.0	15.0	19.0
47	DA-37-17-H600	0.0	2.0	7.0	10.0	15.6
48	DA-37-18-H600	0.0	2.0	9.0	14.0	19.5
49	DA-37-19-H600	1.0	4.0	12.0	17.5	23.0
50	DA-37-20	4.0	10.0	25.0	36.0	45.0
51	DA-37-21	2.0	4.6	20.0	25.0	36.5
52	DA-37-22-H425	0.0	3.0	11.0	14.0	19.0
53	DA-37-23-H425	0.0	3.5	19.0	26.0	32.0
54	DA-37-24	6.0	59.0	68.0	70.0	73.0

Table 10

Loss in Weight of Polymers Postheated to 1176°C

Appendix Number	Polymer	% Loss in Weight on Basis of	
		Reheated Sample	Original Sample
34	DA-37-12-R	3.0	2.0
35	DA-37-12-H425-R	3.8	3.0
36	DA-37-12-H600-R	2.3	2.0
37	DA-37-13-R	3.0	2.0
38	DA-37-13-H425-R	3.8	3.0
39	DA-37-13-H600-R	2.3	2.0
40	DA-37-14-H600-R	2.3	2.0
41	DA-37-15-R	2.0	1.0
42	DA-37-15-H425-R	3.8	3.0
43	DA-37-15-H600-R	2.3	2.0
44	DA-37-16-R	4.5	2.0
45	DA-37-16-H425-R	3.0	2.0
46	DA-37-16-H600-R	5.0	4.0
47	DA-37-17-H600-R	5.0	4.0
48	DA-37-18-H600-R	5.0	4.0
49	DA-37-19-H600-R	6.5	5.0
51	DA-37-21-R	6.0	4.0
52	DA-37-22-H425-R	2.5	2.0
53	DA-37-23-H425-R	1.4	1.0
54	DA-37-24-R	10.0	2.0

c. Recycle in Air.

To contrast the thermal behavior in air of polymers heat-treated to 1176°C with those prepared at 320°C, 425°C and 600°C the polymer samples which had been subjected to 1176°C in the thermogravimetric analyzer were recycled in the apparatus in the presence of air. Preliminary experiments showed that there was no substantial difference in thermal behavior in air between those samples which had been processed once to 1176°C (curve 1 in the thermograms) and those which had been recycled under nitrogen (curve 2 in the thermograms). In the interest of economy of time, the thermoanalysis in air of samples heated to 1176°C were performed on samples which were allowed to remain in the thermogravimetric analyzer after the recycle, that is, the second cycle in nitrogen to 1176°C. Table 8 lists, in column 4, the polymers designated by the appended letter a which were recycled in air to 1176°C after two cycles in nitrogen together with the appendix number of the thermogram in which curve 3 plots the data obtained. Table 11 lists the temperature at which loss of weight begins, the temperature at which 20% of the weight has been lost, and the temperature at which the sample completely disappeared while being heated in air after having been heated to 1176°C in nitrogen.

B. General Discussion.

The data in the thermograms shows that:

(1) The polycondensations performed to 320°C are not complete. This is indicated by the loss in weight when these polymers are heated in nitrogen compared to the much lower losses when the polymers are condensed to higher temperatures. This confirms earlier findings[1-3] on syntheses of poly-Schiff bases by other reagents which did not involve xylylidenetetra-n-butyl ether;

Table 11

Temperatures at Which Weight Loss Begins, Has Occurred to 20%, is Complete While Being Heated in Air After Having Been Heated to 1176°C in Nitrogen

Thermogram Appendix Number	Polymer	Sample Begins to Lose Weight at °C	Sample Has Lost 20% wt. at °C	Sample Has Disappeared at °C
34	DA-37-12	470	600	840
35	DA-37-12-H425	480	620	1000
36	DA-37-12-H600	480	664	1000
37	DA-37-13	520	630	900
38	DA-37-13-H425	500	650	920
39	DA-37-13-H600	540	682	920
40	DA-37-14-H600	530	670	1000
41	DA-37-15	600	695	1000
42	DA-37-15-H425	510	610	800
43	DA-37-15-H600	500	620	840
44	DA-37-16	480	610	740
45	DA-37-16-H425	485	638	738
46	DA-37-16-H600	470	600	880
47	DA-37-17-H600	535	670	880
48	DA-37-18-H600	500	620	840
49	DA-37-19-H600	460	580	800
51	DA-37-21	500	610	680
52	DA-37-22-H425	444	580	805
53	DA-37-23-H425	480	620	860
54	DA-37-24	470	540	700

(2) When condensed to 320°C the heat-resistance of most of the polymers is in the vicinity of 400°C as seen in thermograms of appendix numbers 1, 4, 7, 13, 16, 19, 22, 25, and 29;

(3) When the condensation is carried to 320°C in those polymerizations in which benzalaniline is used as a solvent, the presence of benzalaniline retards the condensation of xylylidenetetra-n-butyl ether with p-phenylenediamine and reduces the heat resistance of the polymer in air. This is shown in the thermogram of appendix 10 in which the condensation is seen to continue as the temperature is raised, in contrast to the behavior of m-phenylenediamine as shown in thermogram of appendix number 2. However, when the condensation up to 320°C involving benzalaniline is performed in the presence of $ZnCl_2$ as a catalyst, the degree of condensation is improved and the heat resistance again rests in the 400°C region as found in the thermogram of appendix numbers 27 and 31;

(4) When the polymers are condensed to a temperature of 425°C, the heat resistance of the polymers in air lies in the 500°C region. The eight polymers shown in thermograms, appendix numbers 2, 5, 8, 11, 14, 20, 23 and 26 are in the 500-550°C range, and the four given in appendix numbers 17, 28, 30 and 32 are in the 475°C to 480°C range. The four polymers of appendix numbers 2, 5, 8 and 20 show heat resistances of 550°C (1022°F) in air;

(5) When benzalaniline is used as a solvent in those condensations carried to 425°C, the heat resistance of these polymers in air lies in the region of 475-500°C and approaches those of polymers prepared in the absence of benzalaniline as shown in the thermograms of appendix numbers 11, 28, 30 and 32. The lower values do show that either chain-end coupling in benzalaniline telomerized polymers is not completed at 425°C for the

time interval studied, or all of the benzalaniline by-product or solvent has not diffused from the polymer;

(6) When the condensation is performed to a temperature of 600°C a number of effects are noted. First, the twenty-minute heating time at 600°C appears to be insufficient, to cause complete condensation in all cases. To assure the maximum degree of polymerization, it would have been preferable[3] to have taken the polymer previously treated to 425°C rather than those heated to 320°C as the sample for treatment to 600°C. Under the specific conditions of these experiments, there is, in the case of the m-phenylenediamine polymers, little or no difference in the heat resistance in air between the polymers treated to 600°C and the 425°C polymers; both show values of 550°C as shown in thermograms of appendix numbers 3 and 6 contrasted to those of numbers 2 and 5. However, in the case of the p-phenylenediamine polymers there is found a reduced heat resistance in air for polymers heated to 600°C for twenty minutes, compared to those heated to 425°C for twenty-four hours; this reduction is noted also in polymers prepared with mixtures of p-phenylenediamine with m-phenylenediamine. These conclusions are supported by a contrast of the thermograms appendix numbers 9, 12, 15, 18 and 21 with numbers 8, 11, 14, 17 and 20. This reduction is attributable to the poorer reactivity of the para derivatives which is aggrevated by the difference in the time schedule of the experiments. The difference under the experimental conditions used points to the m-phenylenediamine as the preferred reactant; also, since the polymers derived from the m- and p-phenylenediamines can be prepared to have substantially the same heat stability of the order of 550°C in air, it does not appear necessary to evaluate polymers prepared from the p-phenylenediamine which have been heated to 600°C in a time schedule which

includes many hours at 425°C. Future studies will be concentrated on the use of m-phenylenediamine and its dibenzylidene derivatives;

(7) The heat resistance of yellow polymers in air is much less than those of the black polymers, as shown in thermogram appendix number 33;

(8) When heated in nitrogen, the thermograms indicate for most of the polymers, that polycondensation, and possibly other types of condensations, continue up to a temperature of 1176°C, which corresponds to a recorded temperature of 1200°C corrected for the non-linearity of the chromel-alumel thermocouple. This continued polycondensation is evident in each of curve number 1 of the thermograms of appendix numbers 34 to 53 inclusive. In most of these thermograms, it will be observed in the weight-temperature plots, that little or no loss in weight is found as the samples are heated to a higher temperature until some definite temperature is reached; there a first distinct negative slope occurs until it reaches a second higher temperature where it tends to level out as a second but smaller negative slope becomes evident which continues to the temperature limit of the apparatus, namely, 1176°C.

The first negative slope can be attributed to losses of by-products due to continued condensation polymerization and the temperature at which it originates depends, as would be expected, on the previous thermal history of the sample. For example, in those polymers which had been polymerized to a temperature of 325°C, the first negative slope is found approximately in the 500-700°C region; in those postheated to 425°C it is in the 600-750°C region and for those postheated to 600°C, it is found in the 700-900°C region.

The second negative slope may be interpreted from the nature of the plots as originating <u>before</u> the factors responsible for the first negative slope are completed and it may be approximated that generally it takes origin in the 800-850°C range. Though the losses in this region may be attributed in part to continued condensation which would be expected to be minor, they also may be due to condensations between polymer chains to yield fused ring structures by loss of hydrogen or other by-products.

An insight into the nature of these reactions can be better obtained by analyzing the gases or products collected during the thermogravimetric run, and by differential thermal analysis by reference to the infrared spectra, if interpretable, of the polymers resulting from such treatment. Such studies are contemplated in future research. In any case, the thermograms performed in nitrogen indicate that condensation polymerization should be continued for a sufficient time to some temperature above 600°C, probably to a temperature in the region of 750-800°C. This will require metal heating blocks capable of withstanding these temperatures; for this purpose, copper, MP $>$ 1000°C, is satisfactory. It would also require a new design or structure in the means of heating this copper block and of maintaining the desired temperature thermostatically.

It is interesting to note the appearance of the polymers after heating to 1176°C in nitrogen; the finely powdered samples have the appearance of relatively shiny, very black particles of the original shape, and not of a dusty, powdery product characteristic usually of carbonized polymers. The yellow brick-dust polymer, DA-37-24, appendix number 54, also became black but it retained a brick-dust character;

(9) When any or all of the polymers which have been heated to 1176°C in nitrogen in the thermogravimetric apparatus are recycled under nitrogen there is no evidence of further condensations of any kind as indicated by the substantially linear plot of weight versus temperature in each curve 2

of the thermograms of appendix numbers 34 to 49, and 51 to 54 inclusive. This means that by pretreating the polymers in an inert atmosphere at temperatures in excess of 800°C, for example, in the range of 800-1100°C, a polymer is obtained which shows heat stability in nitrogen or inert atmosphere to 1176°C. At the present time, it is not known whether or not the nitrogen reacts with the polymers at these temperatures. Accordingly it is intended in future research to evaluate helium as the inert atmosphere relative to nitrogen, and to perform some of the thermograms at reduced pressures;

(10) When any or all of the polymers which have been heated to 1176°C in nitrogen in the thermogravimetric apparatus are recycled in air as shown in each curve 3 of the thermograms of appendix numbers 34 to 49 and 51-53 inclusive, all showed heat stabilities in air in excess of 500°C with a spread in temperature range of 500-600°C. Two polymers, the meta-polymer DA-37-13-H600 (Appendix No. 39) and the para-polymer, DA-37-15-H600 (Appendix No. 41) showed remarkable stability to 600°C (1112°F) in air. This is interpreted to mean that if the polycondensations are complete, as they must be at the temperature used in the preheating, that the meta- and para-polymers are substantially identical and that when benzalaniline is used as a solvent, as it was in DA-37-15-H600, it is substantially eliminated even as telomerized end groups;

(11) When the polymer is meant for use in air, there is only a difference of about 50°C in the heat stability of a polymer condensed to a temperature in the region of 600°C (or to some slightly higher temperature to be chosen after more studies, for example, 750-800°C) and one condensed to 1176°C. Whereas, if use is intended for the polymers in an inert atmosphere to temperatures in excess of 600°C, the polycondensation should be performed to temperatures of the order of 800°C or higher.

(12) The yellow brick-dust polymers have lower heat resistance in nitrogen and air than the black polymers, even after postheating in nitrogen twice to 1176°C;

(13) The polymers prepared from p-xylylidenetetra-n-butyl ether and the m- or p-phenylenediamines or their dibenzylidene derivative appear to be identical, except for end groups, to the polymeric Schiff bases prepared by Schiff base exchange reactions.[1-3]

V. Summary and Conclusions.

1. Black polymeric Schiff bases which pass through a fusible stage can be made from p-xylylidenetetra-n-butyl ether and either m- or p-phenylenediamine or their dibenzylidene derivates in the absence or presence of benzalaniline as a solvent. Differences between the resulting polymers are not great.
2. The synthesis of the Schiff base polymers is smoother with m-phenylenediamine and its dibenzylidene derivative than from p-phenylenediamine and its benzylidene derivative. The cost of m-phenylenediamine is much lower than the para compound and its use is preferred and recommended.
3. The polymers prepared from m-phenylenediamine and xylylidenetetra-n-butyl ether have heat-resistant properties at least as good as those prepared from p-phenylenediamine.
4. Polymers condensed to temperatures of 425°C to 600°C show a heat resistance in air of 525-550°C. This temperature range appears to be the region in which combustion of the by-products of condensation begin to burn.
5. Polymers condensed at temperatures to 1176°C show heat resistance in air of 600°C (1112°F). This appears to be the temperature

region in which combustion of the polymer occurs.

6. Polymers condensed to a temperature of 1176°C (2026°F) show a heat resistance in nitrogen of about 1176°C (2026°F).
7. The experimental work points to other needed areas of study.

VI. Future Research.

1. Establish the best overall conditions for the condensation polymerization of p-xylylidenetetra-n-butyl ether with m-phenylenediamine within the following reaction parameters:
   - a) without and with $ZnCl_2$ catalysis
   - b) without and with benzalaniline as a solvent
   - c) establish temperature range of reaction
   - d) establish time limits of reaction.
2. Compare the behavior of p-xylylidenetetra-n-butyl ether with
   - a) p-xylylidenetetraethyl ether
   - b) the p-xylylidenetetrapropyl ethers.
3. Perform kinetic studies to determine rates of reactions on selected polymers obtained under VI.1 and VI.2.
4. Perform differential thermal analyses on selected polymers obtained under VI.1 and VI.2.
5. Study the postheating to the region of 800°C to 1000°C of polymers prepared to temperatures of about 600°C to determine what changes occur in the polymers, by
   - a) changes in the IR spectra of the polymers
   - b) mass-spectra analyses of by-products of reactions.
6. Determine best point in the polymerization at which the fusible polymer should be isolated for conversion to infusible condition

   a) evaluate use of Lewis acid in the process of conversion to infusibility.

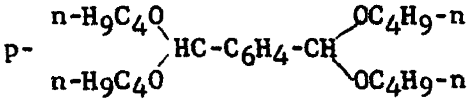
7. Undertake appropriate physical studies involving the following solid state properties of selected polymers and to correlate these properties by
   a) semi-conductor measurements as a function of temperature and conformance to Ohm's law.
   b) electron spin resonance measurements as a function of temperature and relationship to number of free electrons to conductivity.
   c) Heat capacity measurements as a function of temperature for correlation to conductivity and ESR.

VII. Acknowledgment.

The authors and the University of Notre Dame acknowledge gratefully the financial assistance under NASA Grant NsG339 which made this research possible. Appreciated also is the general guidance and assistance given by Mr. Bernard Achhammer, NASA Headquarters, Washington, D. C. 20546.

Thanks are due to James Crivello for assistance in obtaining the thermogravimetric analyses.

VIII. Glossary.

XTBE	 $p\text{-}(n\text{-}H_9C_4O)_2HC\text{-}C_6H_4\text{-}CH(OC_4H_9\text{-}n)_2$
PDA	m- and/or $p\text{-}C_6H_4(NH)_2$
MPDA	$m\text{-}H_2NC_6H_4NH_2$
PPDA	$p\text{-}H_2NC_6H_4NH_2$
BA	$C_6H_5CH{=}NC_6H_5$
DBMPD	$m\text{-}C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$
DBPPD	$p\text{-}C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$

IX. Bibliography.

1. G. F. D'Alelio, T. Kurosaki and J. Crivello, "Fundamental Studies on the Synthesis of Heat-Resistant Polymers." Report No. 5, April, 1965, under NASA Grant NsG339.

2. G. F. D'Alelio, L. Mallavarapu, T. Huemmer, T. Kurosaki, W. Fessler and J. Crivello, "Fundamental Studies on the Synthesis of Heat-Resistant Polymers." Report No. 4, September 15, 1964, under NASA Grant NsG339.

3. G. F. D'Alelio and J. Crivello, "Fundamental Studies on the Synthesis of Heat-Resistant Polymers," The Synthesis and Evaluation of Polymeric Schiff Bases by Bis-Schiff Base Exchange Reactions, Report No. 6, September 15, 1965, under NASA Grant NsG339.

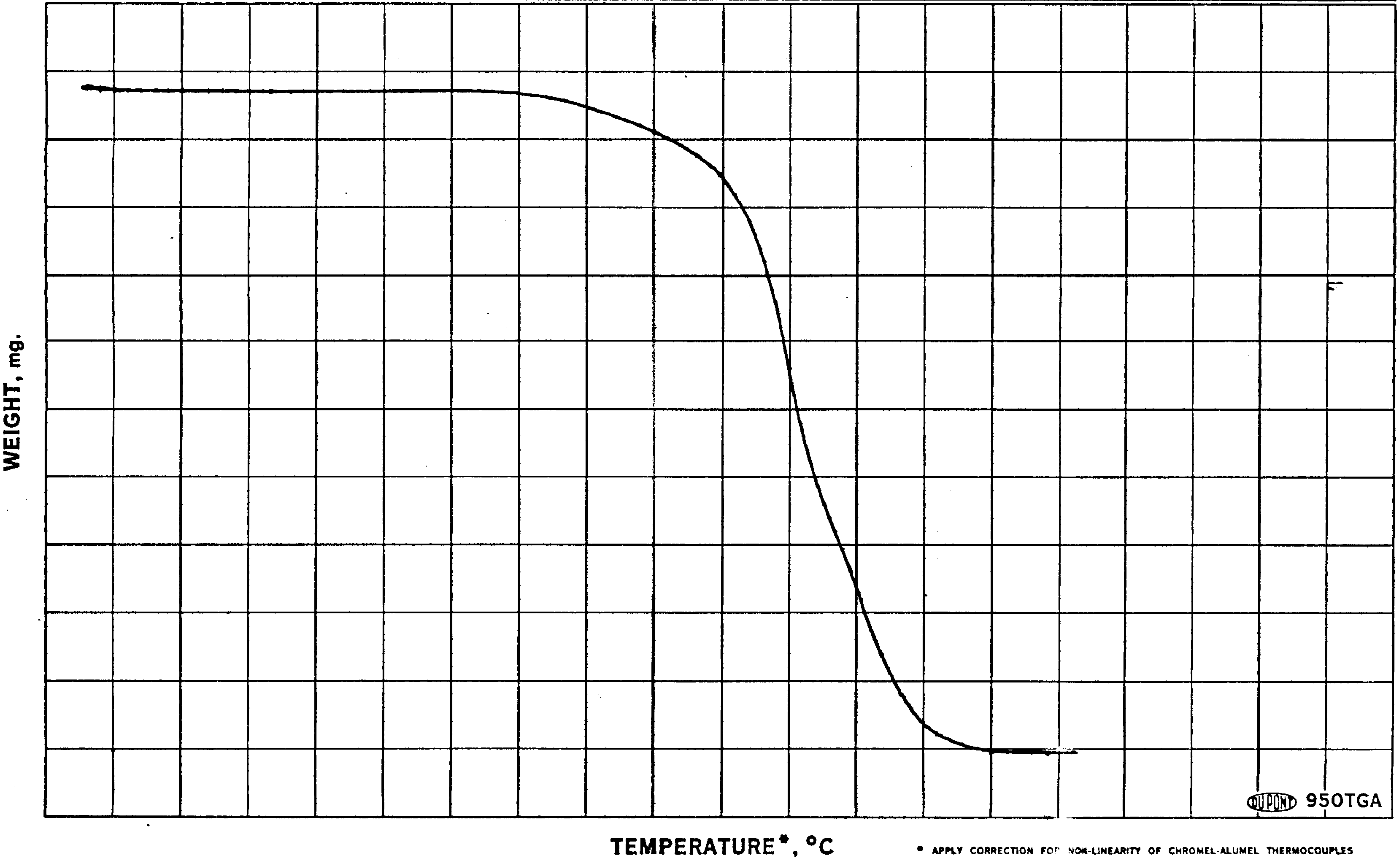
Appendix No. 1

SAMPLE: DA-37-12
m-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
$C_6H_5N\text{-}CHC_6H_5$
SIZE 10 mg.

X-AXIS
TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

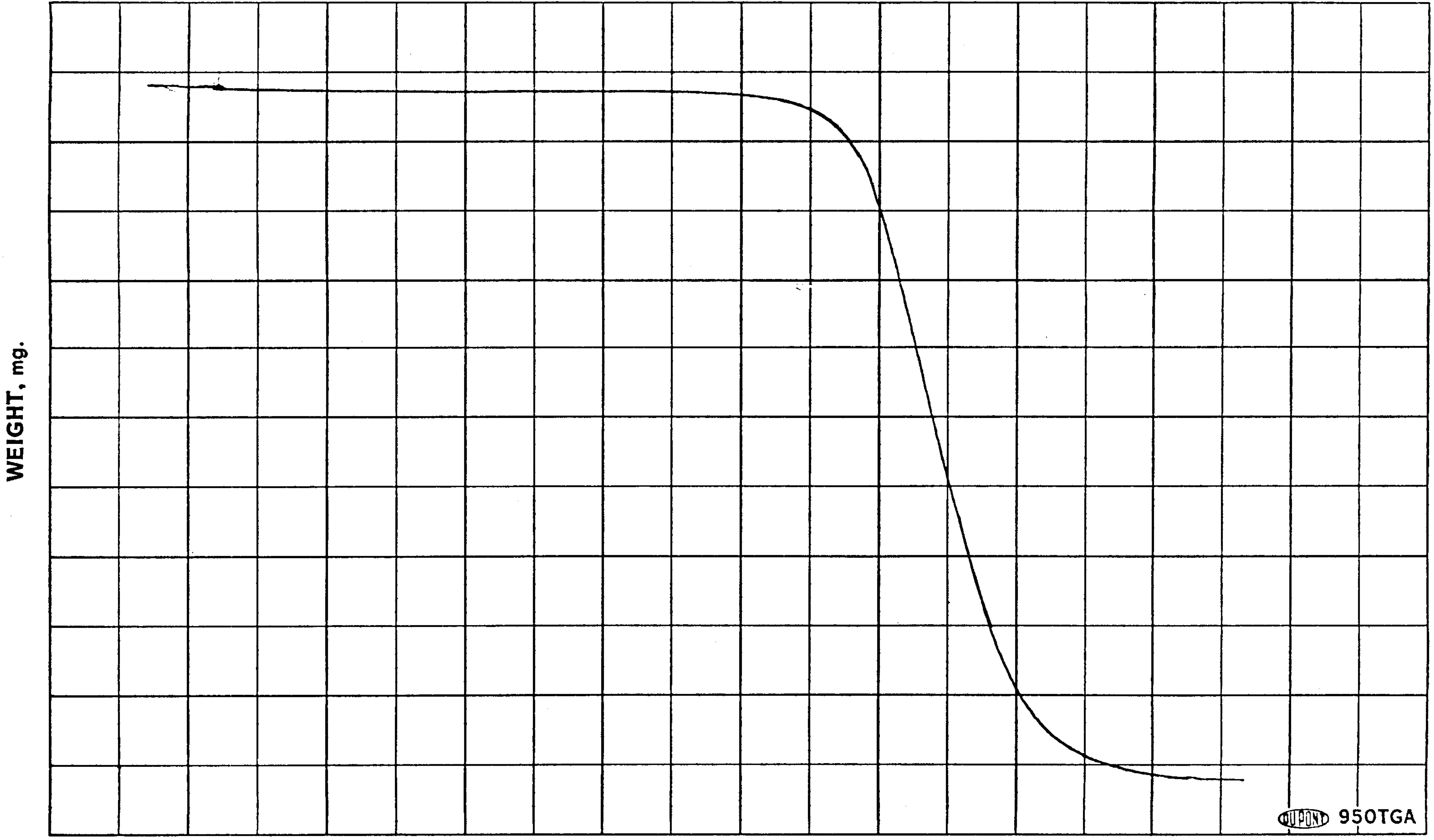
RUN NO. **DATE** 7-25-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 2

SAMPLE: DA-37-12-H425	**X-AXIS**	**Y-AXIS**	**RUN NO.** ______ **DATE** 7-27-65
m-$(H_2N)_2C_6H_4$	**TEMP. SCALE** 100 °C/inch	**SCALE** 2 mg./inch	**OPERATOR** TO
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$	**SHIFT** 0 inch	(SCALE SETTING X 2)	**HEATING RATE** 15 °C/min.
$C_6H_5N{=}CHC_6H_5$			**ATM.** air
SIZE 10 mg.	**TIME SCALE (ALT.)** 0	**SUPPRESSION** 0 mg.	**TIME CONSTANT** 2 sec.



TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 3

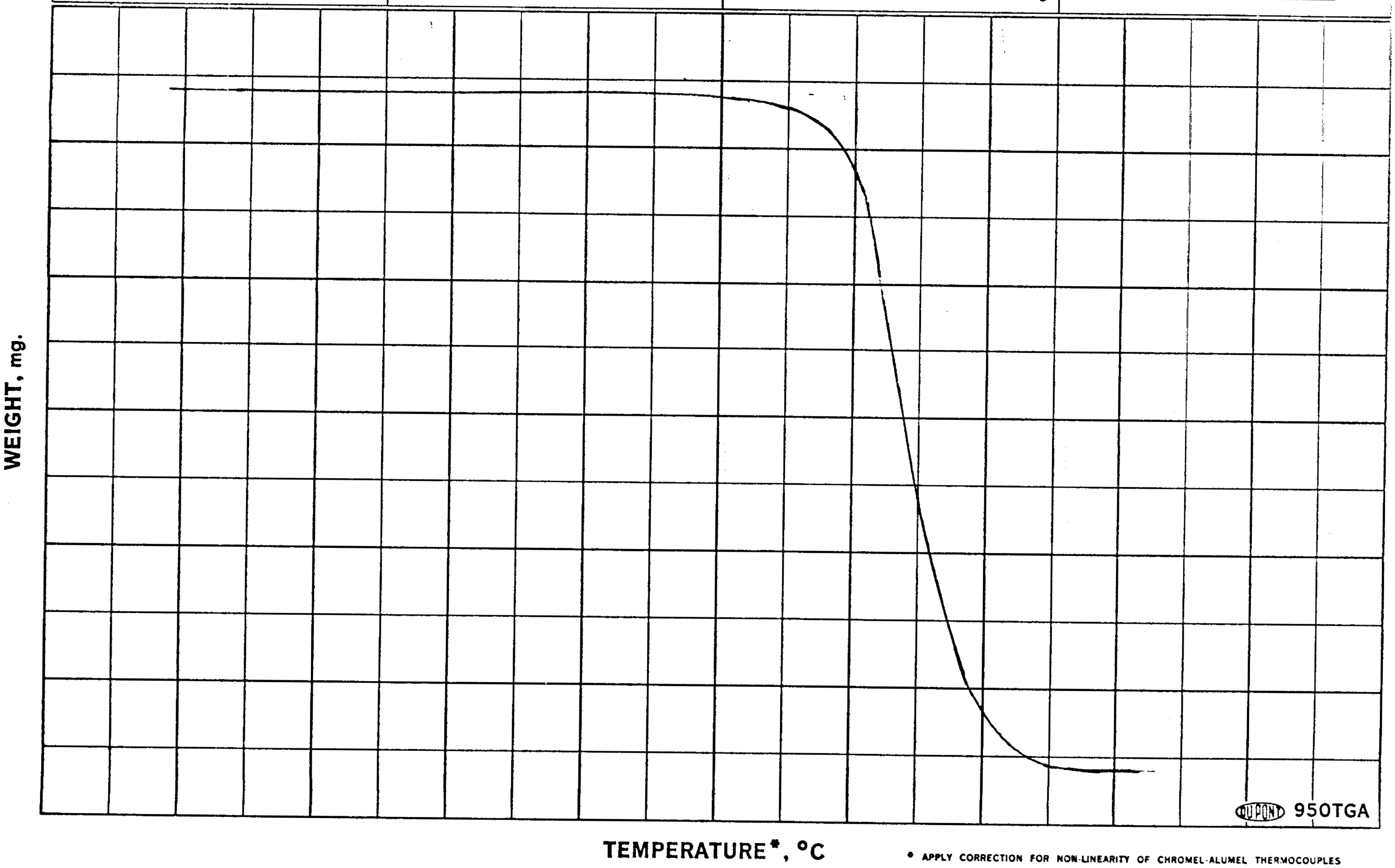
DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-37-12-H600
m-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
$C_6H_5N{=}CHC_6H_5$
SIZE 10 mg.

X-AXIS
TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

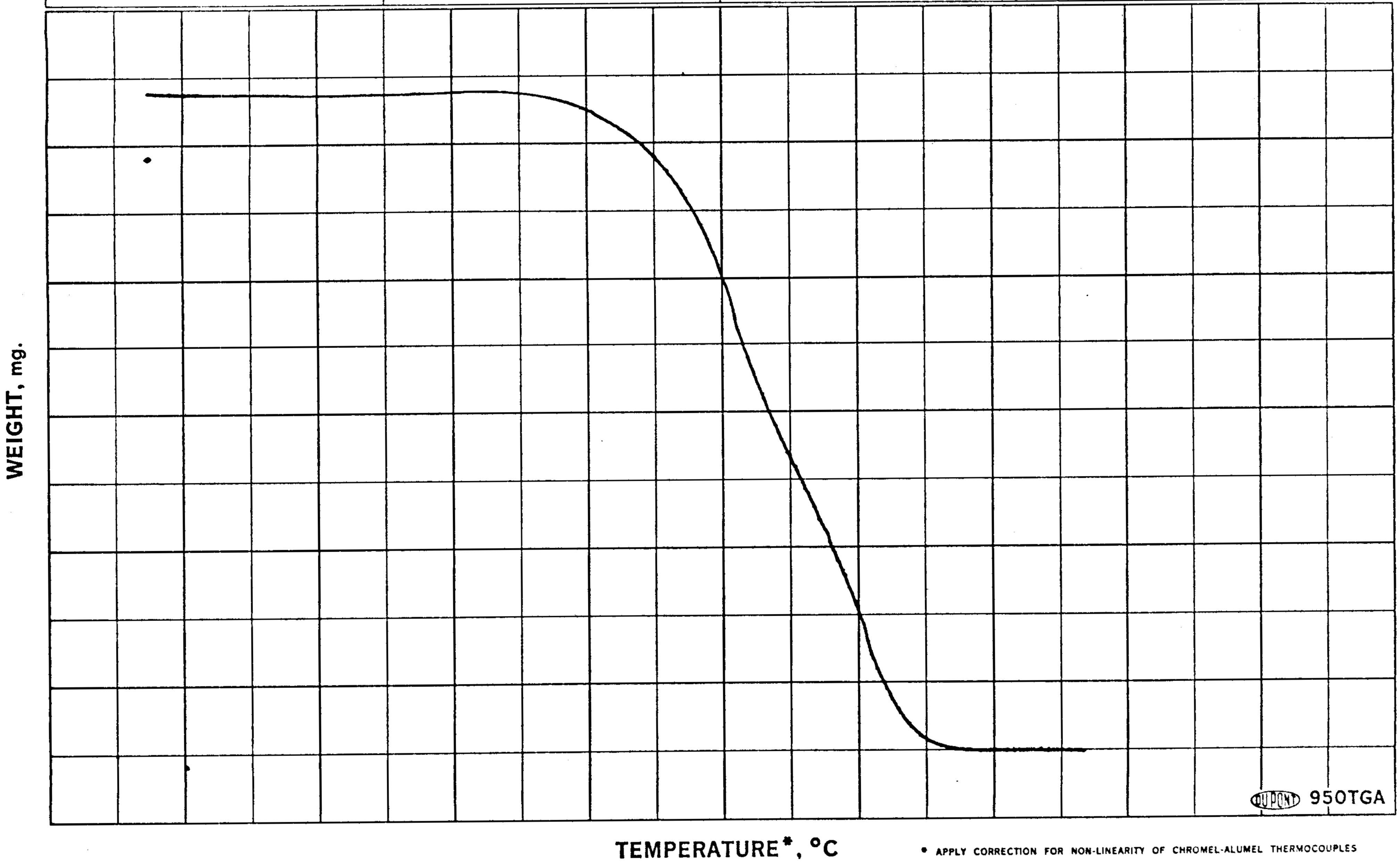
Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. **DATE** 7-27-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

SAMPLE: DA-37-13 m-$(H_2N)_2C_6H_4$ p-$(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent	**X-AXIS**	**Y-AXIS**	RUN NO. ______ DATE 7-22-65
	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR TO
	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. air
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-37-13-H425
m-(H$_2$[illegible])$_2$C$_6$H$_4$
p-[(n-[illegible]O)$_2$CH]$_2$C$_6$H$_4$
no solvent

SIZE 10 mg.

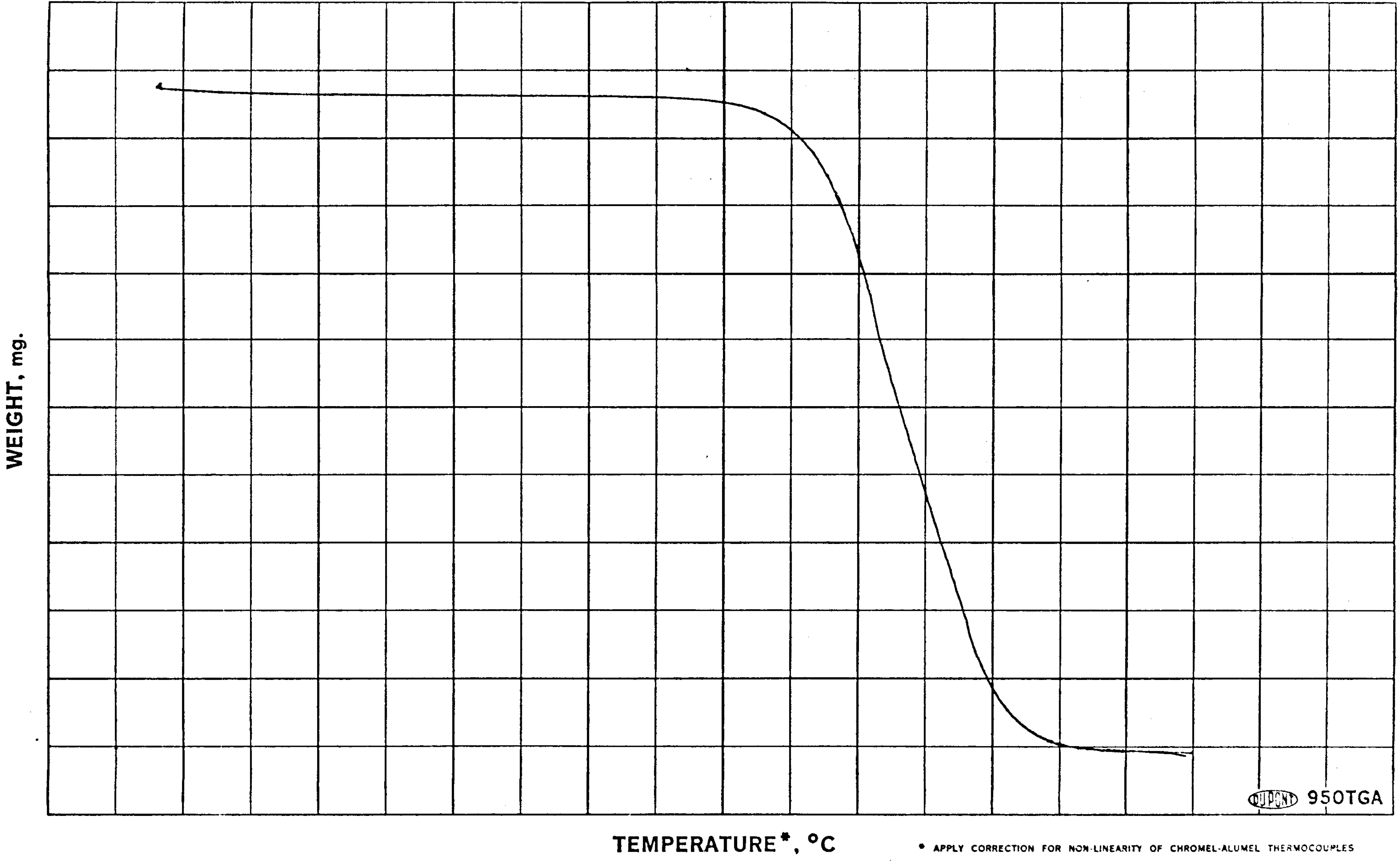
X-AXIS

TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS

SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. **DATE** 7-27-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.

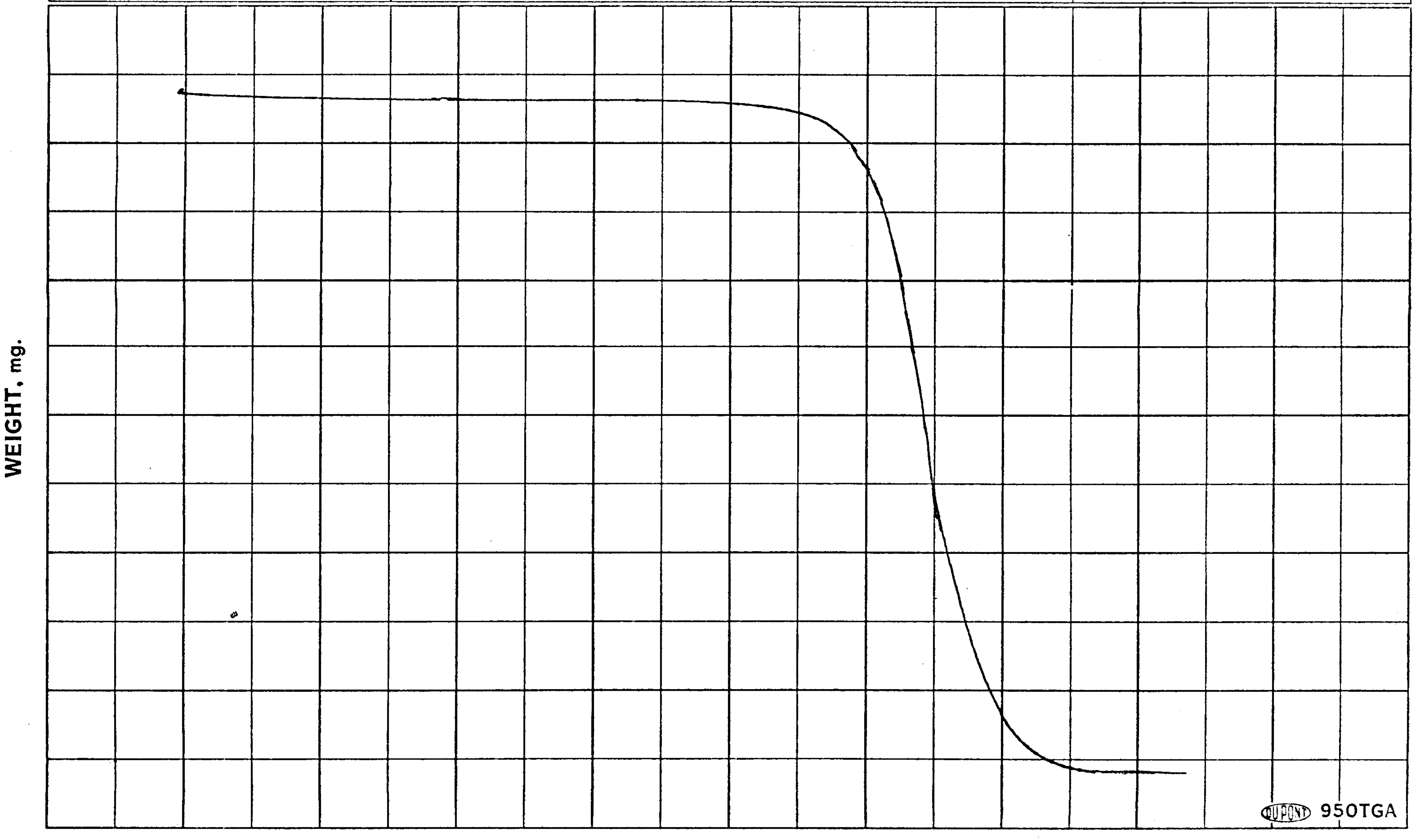


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 5

Appendix No. 6

SAMPLE: DA-37-13-H600 (bottom) m-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent	**X-AXIS**	**Y-AXIS**	**RUN NO.** ______ **DATE** 7-27-65
	TEMP. SCALE 100 °C/inch	**SCALE** 2 mg./inch **(SCALE SETTING X 2)**	**OPERATOR** TO
	SHIFT 0 inch		**HEATING RATE** 15 °C/min.
			ATM. air
SIZE 10 mg.	**TIME SCALE (ALT.)** 0	**SUPPRESSION** 0 mg.	**TIME CONSTANT** 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-14
50 mole % m-$(H_2N)_2C_6H_4$
50 mole % p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
SIZE 10 mg.

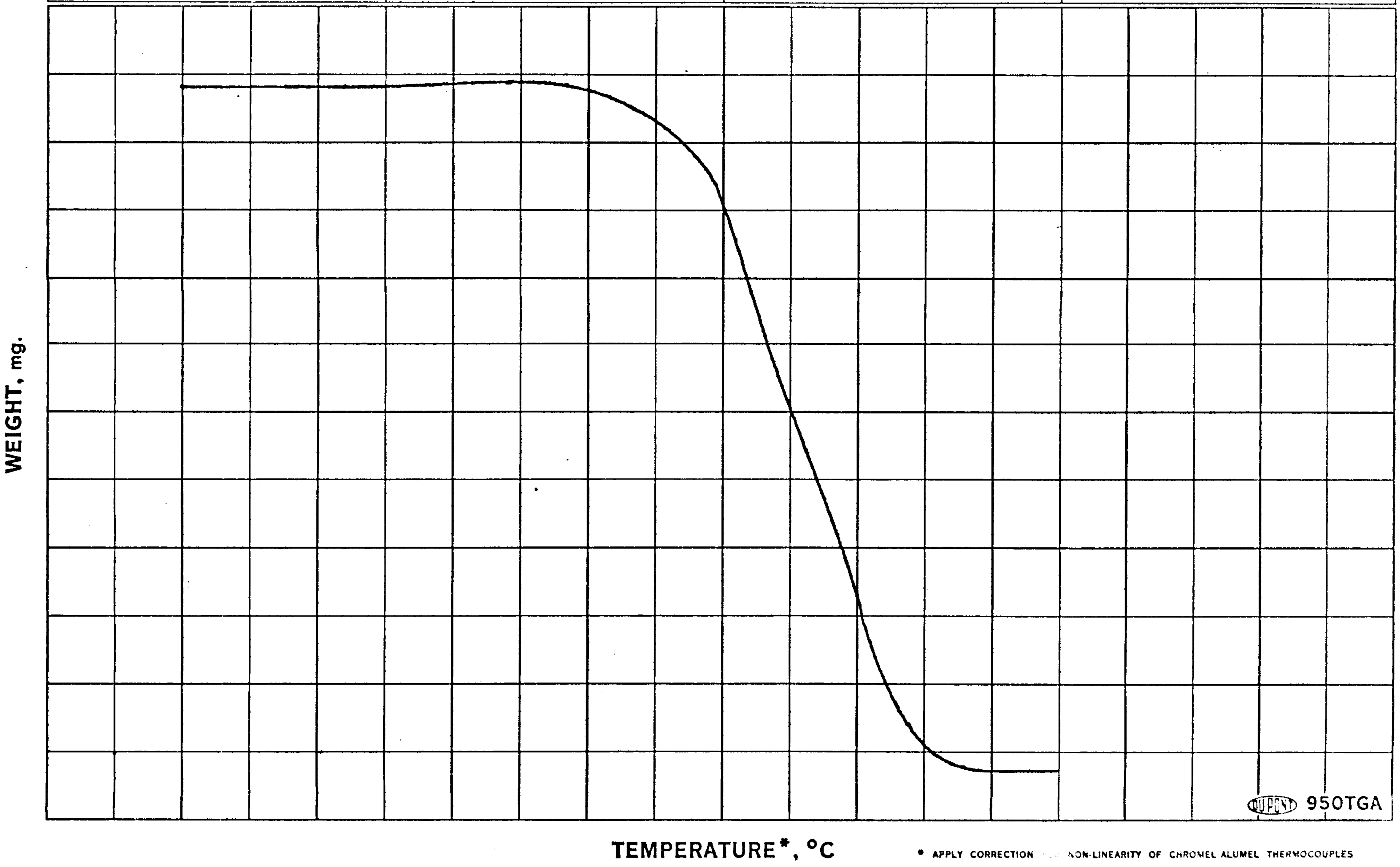
X-AXIS

TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS

SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. **DATE** 7-25-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

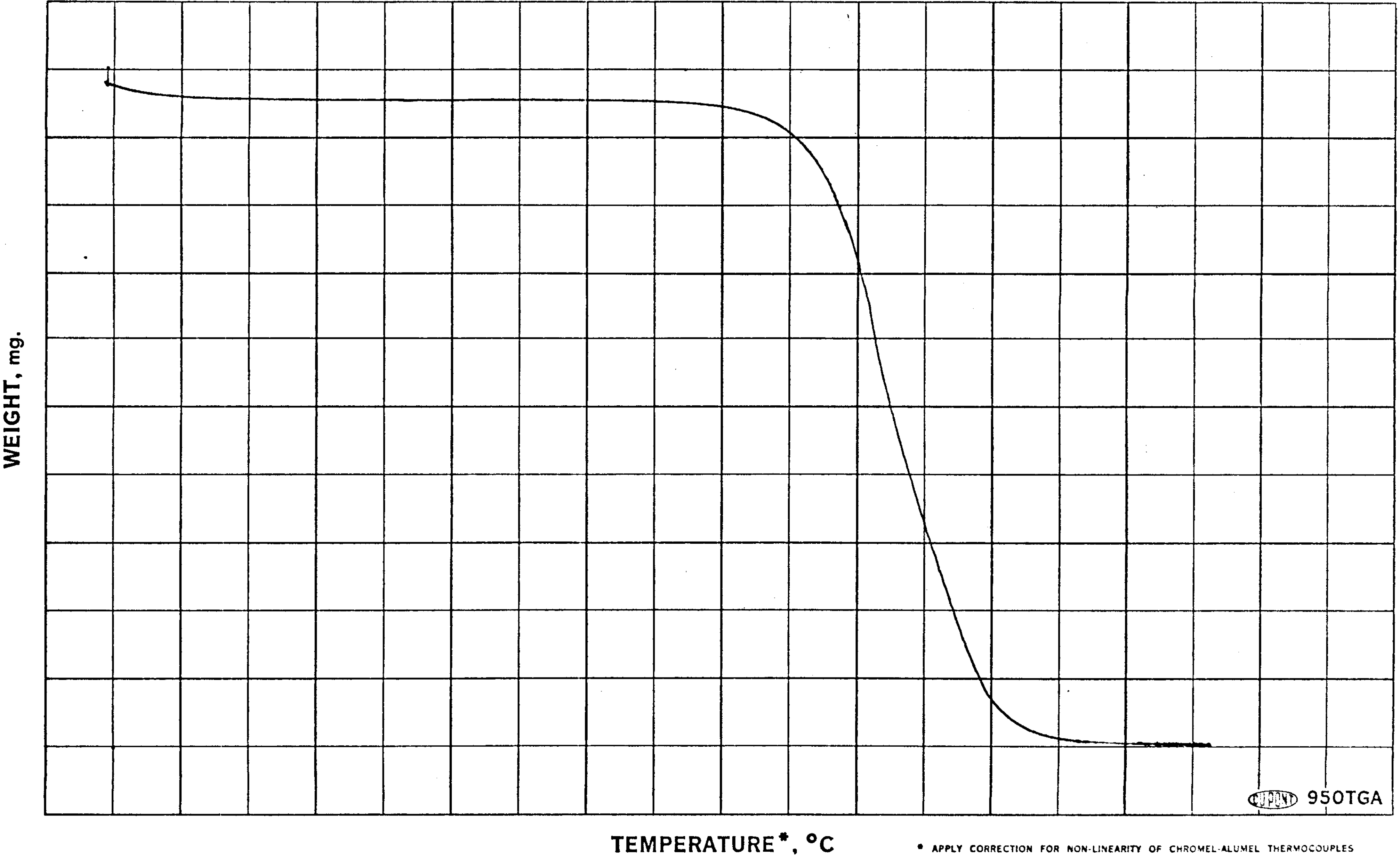
DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-37-14-H425
50 mole % m-$(H_2N)_2C_6H_4$
50 mole % p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
SIZE 10 mg.

X-AXIS
TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

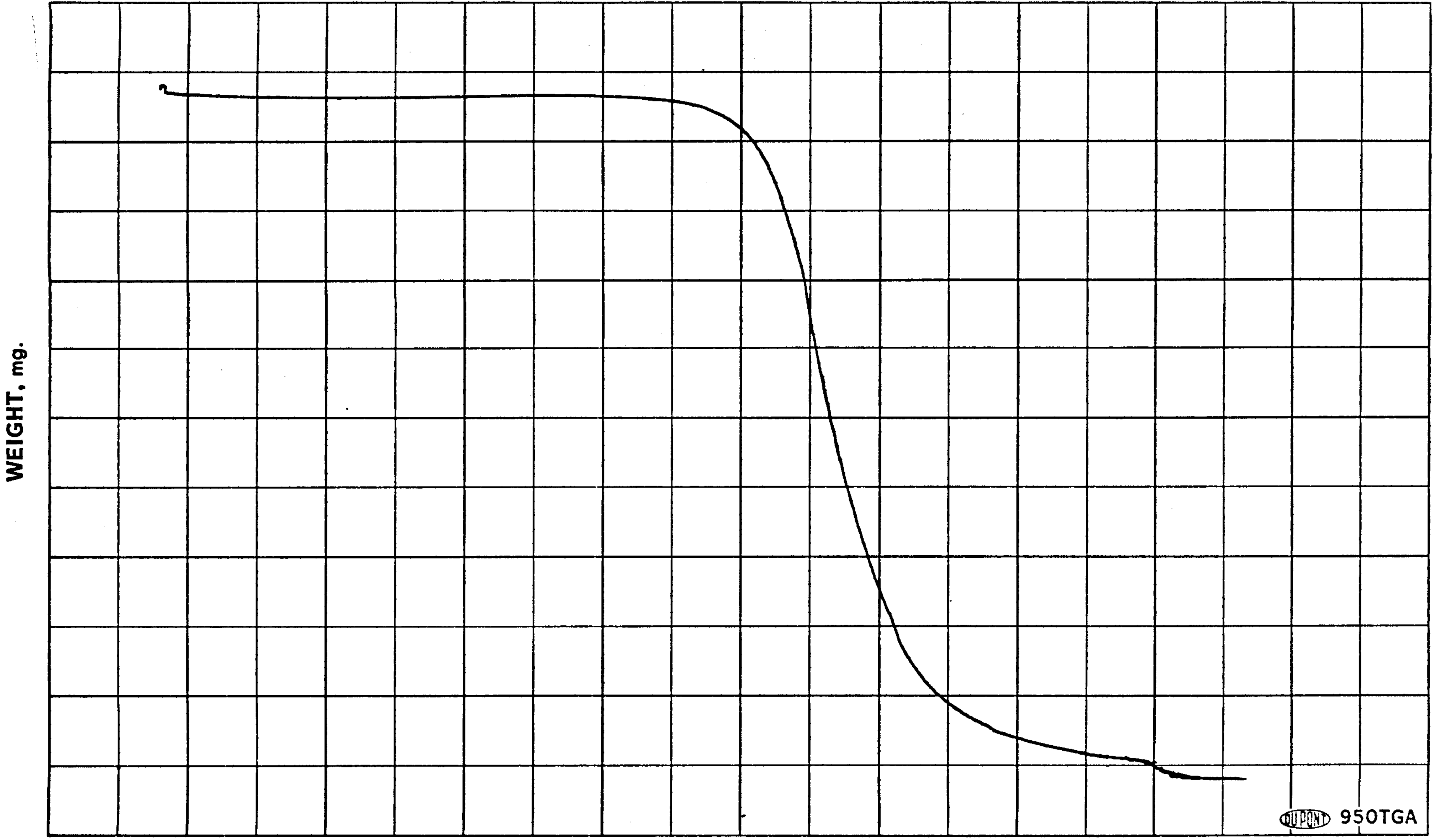
RUN NO. **DATE** 7-27-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 9

SAMPLE: DA-37-14-H600 50 mole % m-$(H_2N)_2C_6H_4$ 50 mole % p-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent	**X-AXIS**	**Y-AXIS**	**RUN NO.** ____ **DATE** 8-4-65
	TEMP. SCALE 100 °C/inch	**SCALE** 2 mg./inch **(SCALE SETTING X 2)**	**OPERATOR** TO
	SHIFT 0 inch		**HEATING RATE** 15 °C/min.
			ATM. air
SIZE 10 mg.	**TIME SCALE (ALT.)** 0	**SUPPRESSION** 0 mg.	**TIME CONSTANT** 2 sec.



TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 10

SAMPLE: DA-37-15
$p\text{-}(H_2N)_2C_6H_4$
$p\text{-}[(n\text{-}BuO)_2CH]_2C_6H_4$
$C_6H_5\text{-}N{=}CHC_6H_5$

SIZE 10 mg.

X-AXIS

TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS

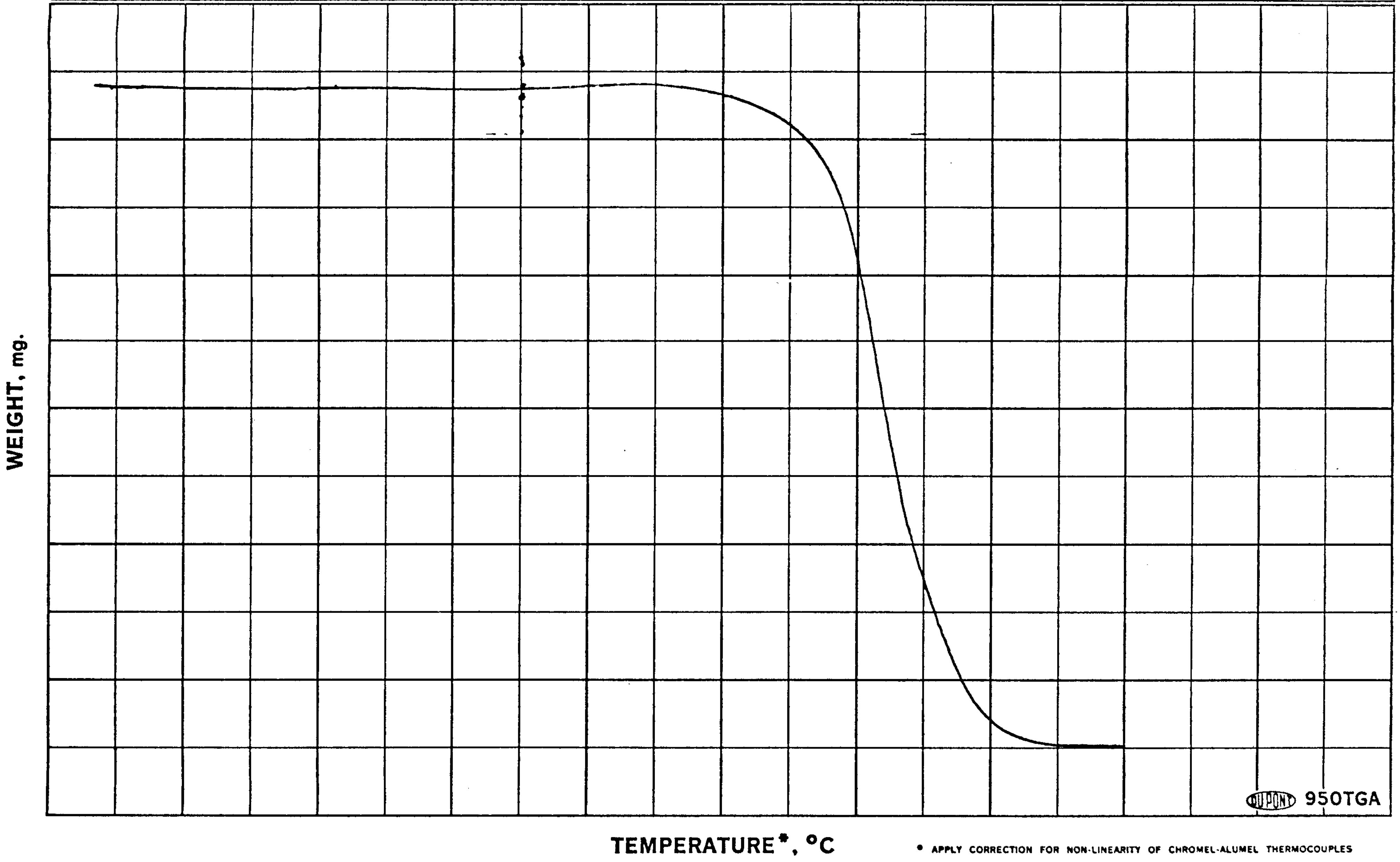
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO.
DATE 7-22-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 11

SAMPLE: DA-37-15-H425 p-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ $C_6H_5N{=}CHC_6H_5$ SIZE 10 mg.	X-AXIS TEMP. SCALE 100 °C/inch SHIFT 0 inch TIME SCALE (ALT.) 0	Y-AXIS SCALE 2 mg./inch (SCALE SETTING X 2) SUPPRESSION 0 mg.	RUN NO. DATE 7-27-65 OPERATOR TO HEATING RATE 15 °C/min. ATM. air TIME CONSTANT 2 sec.



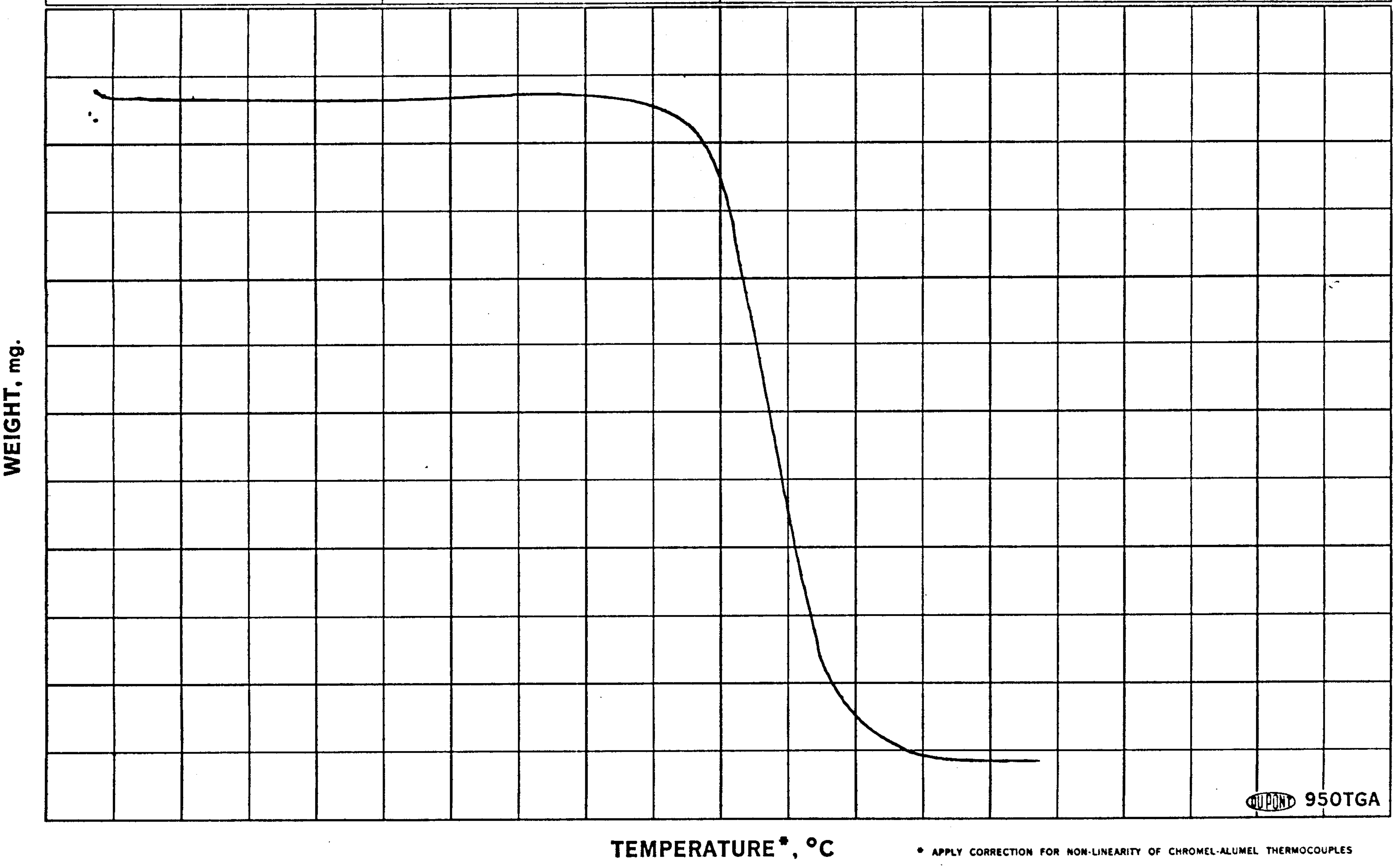
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

SAMPLE: DA-37-15-H600
p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
$C_6H_5CH{=}NC_6H_5$
SIZE 10 mg.

X-AXIS
TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. **DATE** 8-4-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.

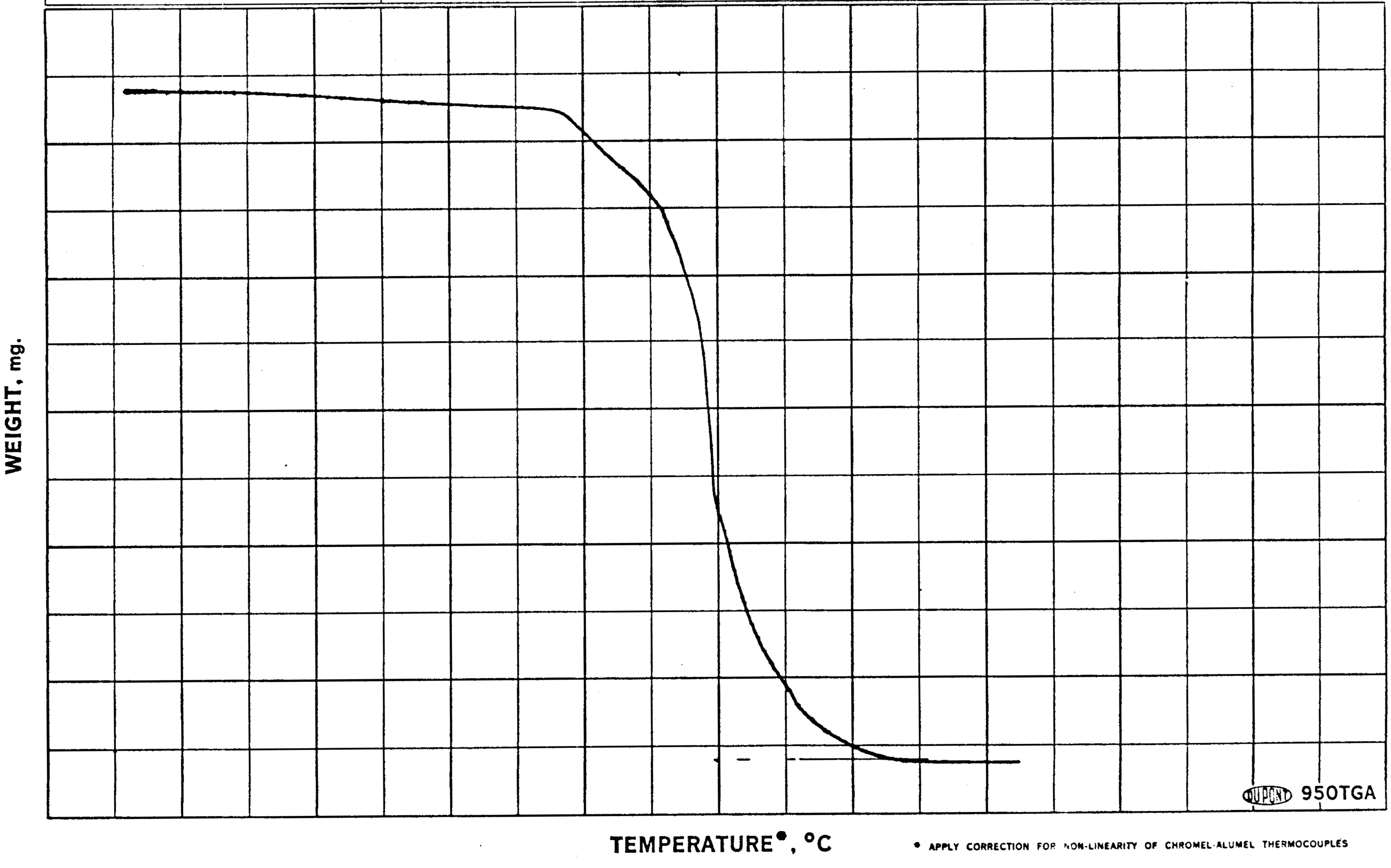


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 13

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-16 p-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent	**X-AXIS**	**Y-AXIS**	RUN NO. ______ DATE 7-22-65
	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR TO
	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. air
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.

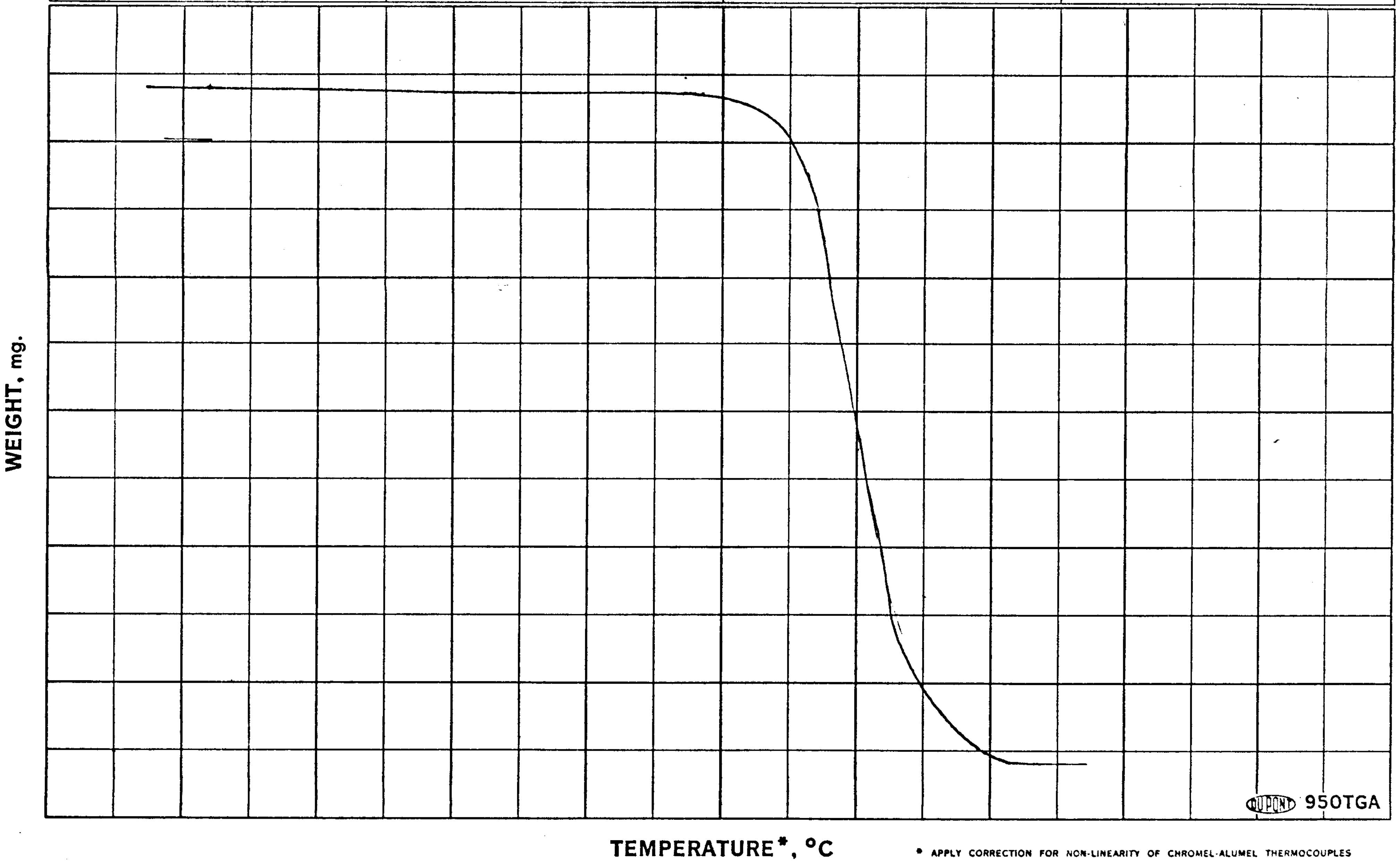


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 14

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-16-H425 p-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent	**X-AXIS**	**Y-AXIS**	**RUN NO.** ______ **DATE** 7-27-65
	TEMP. SCALE 100 °C/inch	**SCALE** 2 mg./inch (SCALE SETTING X 2)	**OPERATOR** TO
	SHIFT 0 inch		**HEATING RATE** 15 °C/min.
SIZE 10 mg.	**TIME SCALE (ALT.)** 0	**SUPPRESSION** 0 mg.	**ATM.** air
			TIME CONSTANT 2 sec.

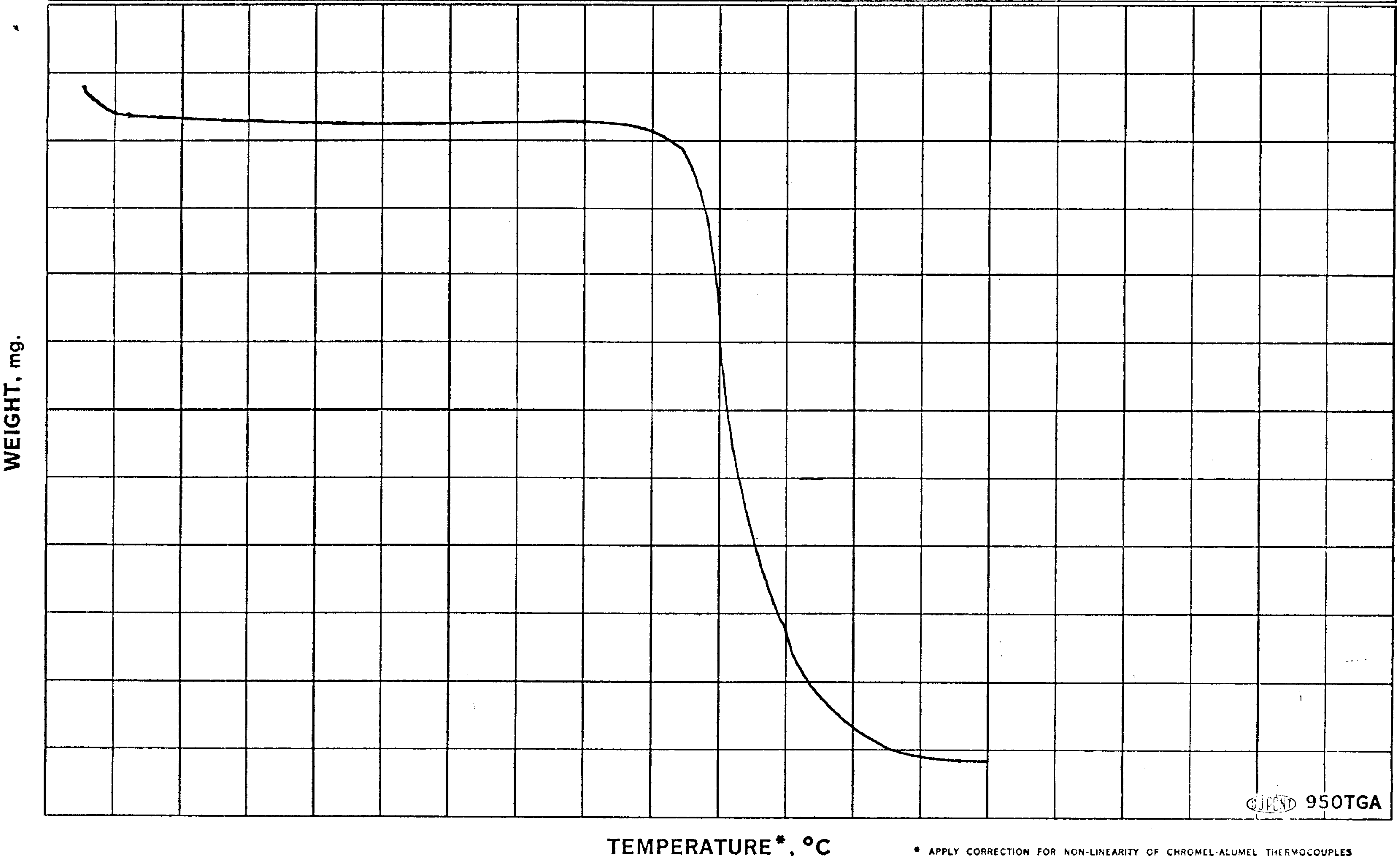


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 15

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-16-H600 p-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent	**X-AXIS**	**Y-AXIS**	**RUN NO.** ____ **DATE** 8-4-65
	TEMP. SCALE 100 °C/inch	**SCALE** 2 mg./inch (SCALE SETTING X 2)	**OPERATOR** TO
	SHIFT 0 inch		**HEATING RATE** 15 °C/min.
			ATM. air
SIZE 10 mg.	**TIME SCALE (ALT.)** 0	**SUPPRESSION** 0 mg.	**TIME CONSTANT** 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

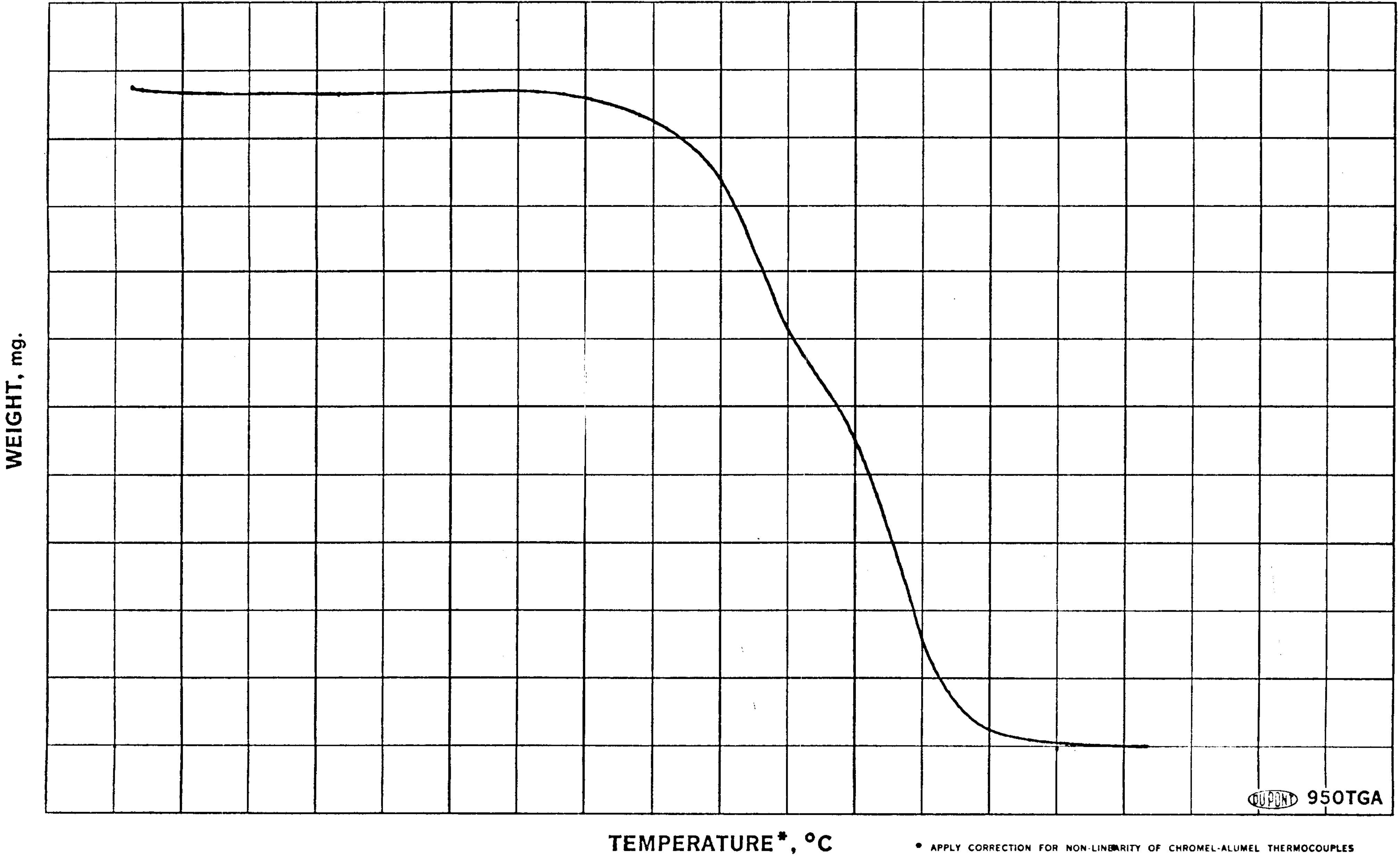
E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-17
25 mole % p-$(H_2N)_2C_6H_4$
75 mole % m-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
SIZE 10 mg.

X-AXIS
TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

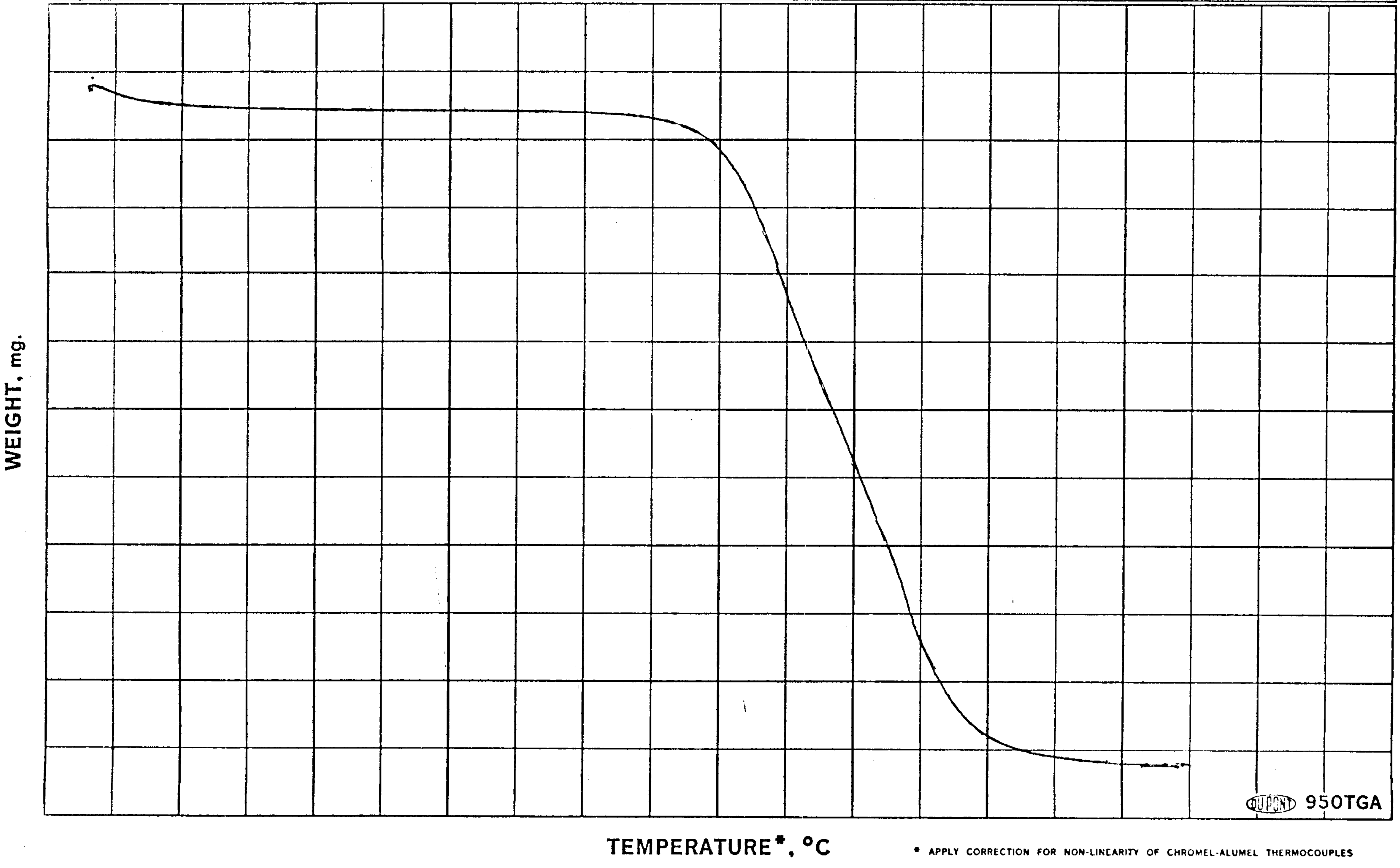
RUN NO.
DATE 7-25-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-17-H425 25 mole % p-$(H_2N)_2C_6H_4$ 75 mole % m-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent	**X-AXIS**	**Y-AXIS**	RUN NO. ____ DATE 7-27-65
	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR TO
	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. air
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 18

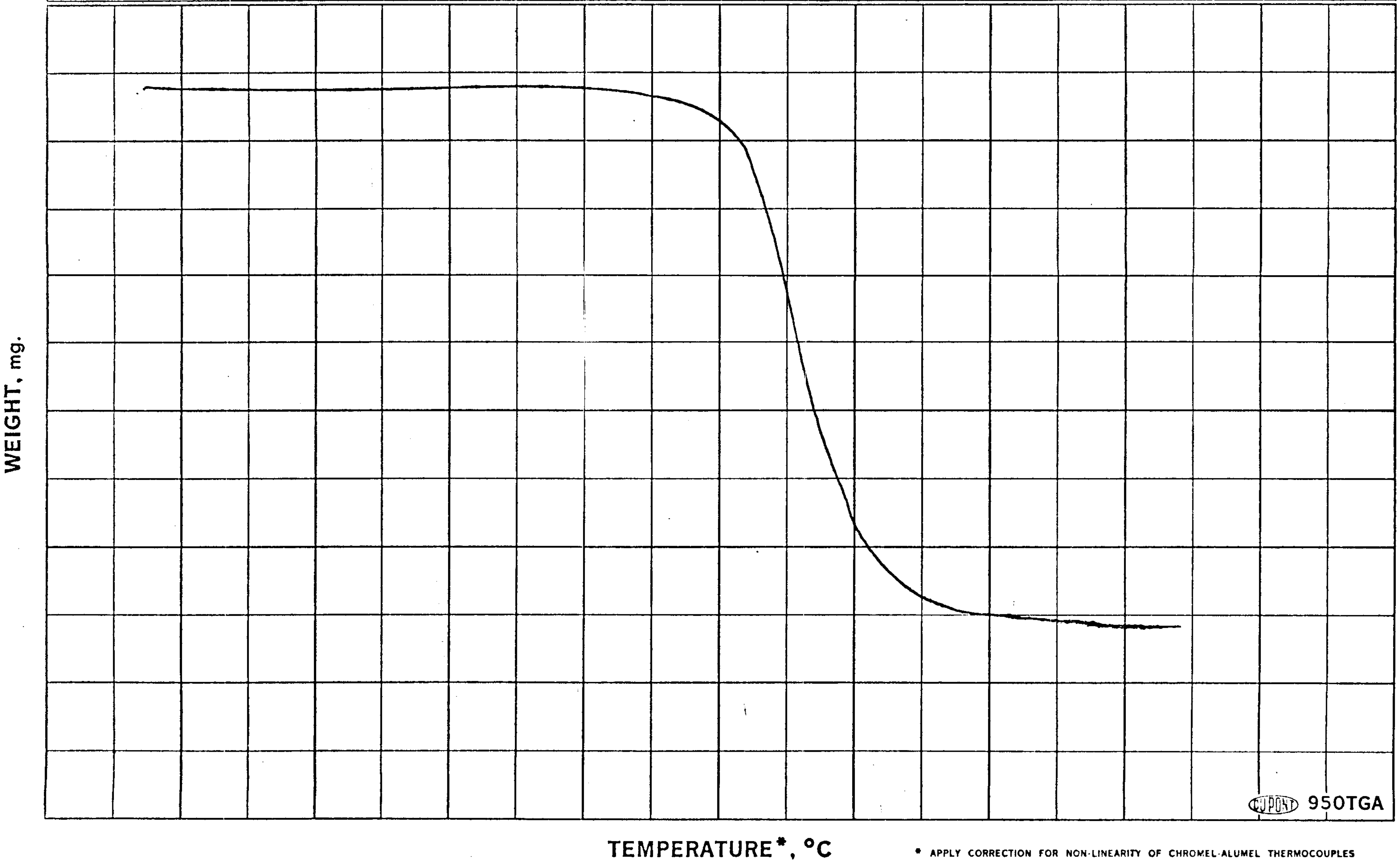
E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-17-H600
25 mole % m-$(H_2N)_2C_6H_4$
75 mole % p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
SIZE 8 mg.

X-AXIS
TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. DATE 7-4-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 19

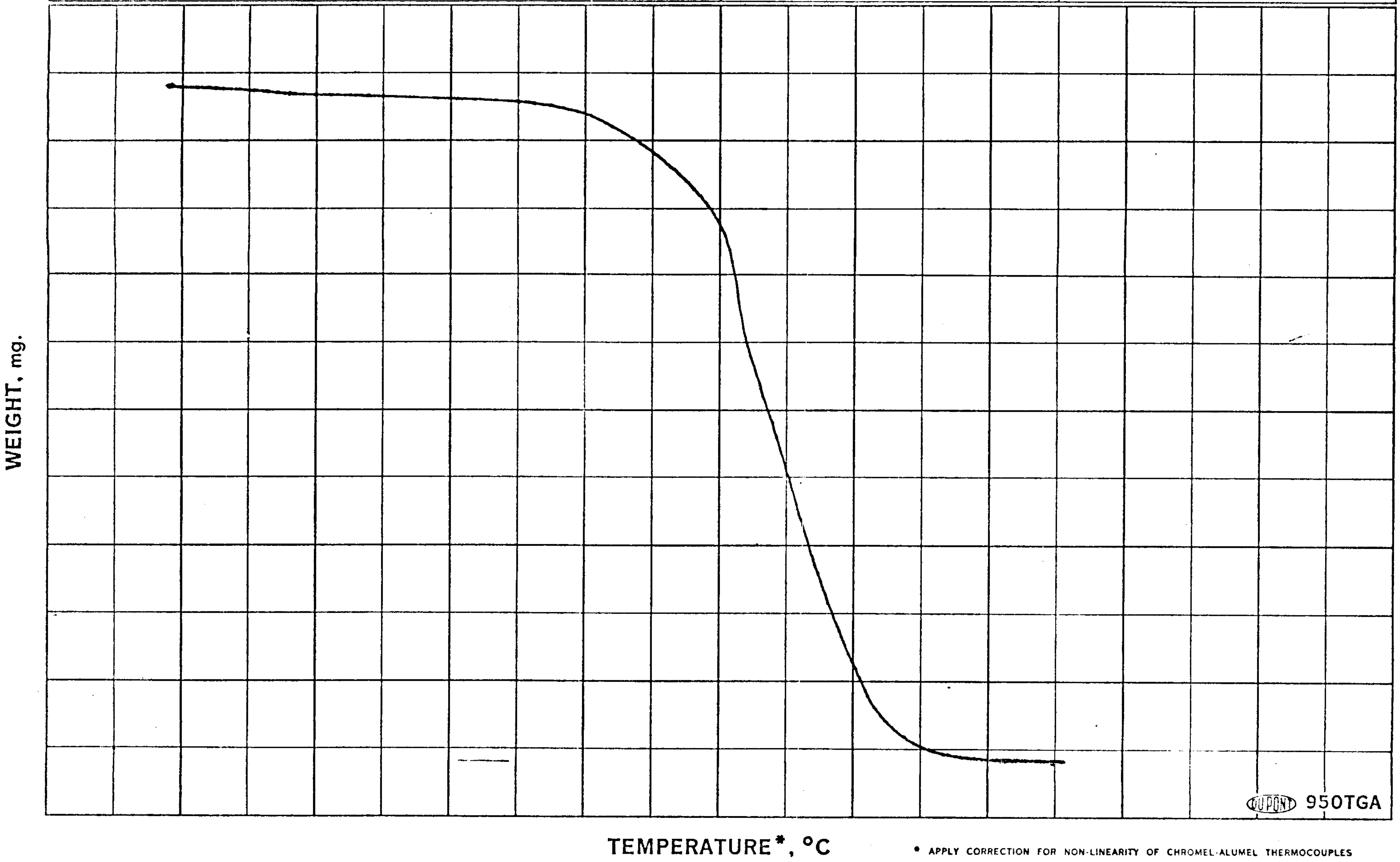
E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-18
25 mole % m-$(H_2N)_2C_6H_4$
75 mole % p-$(H_2N)_2C_6H_4$
p-[(n-BuO)$_2$CH]$_2C_6H_4$
no solvent
SIZE 10 mg.

X-AXIS
TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO.
DATE 7-25-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.

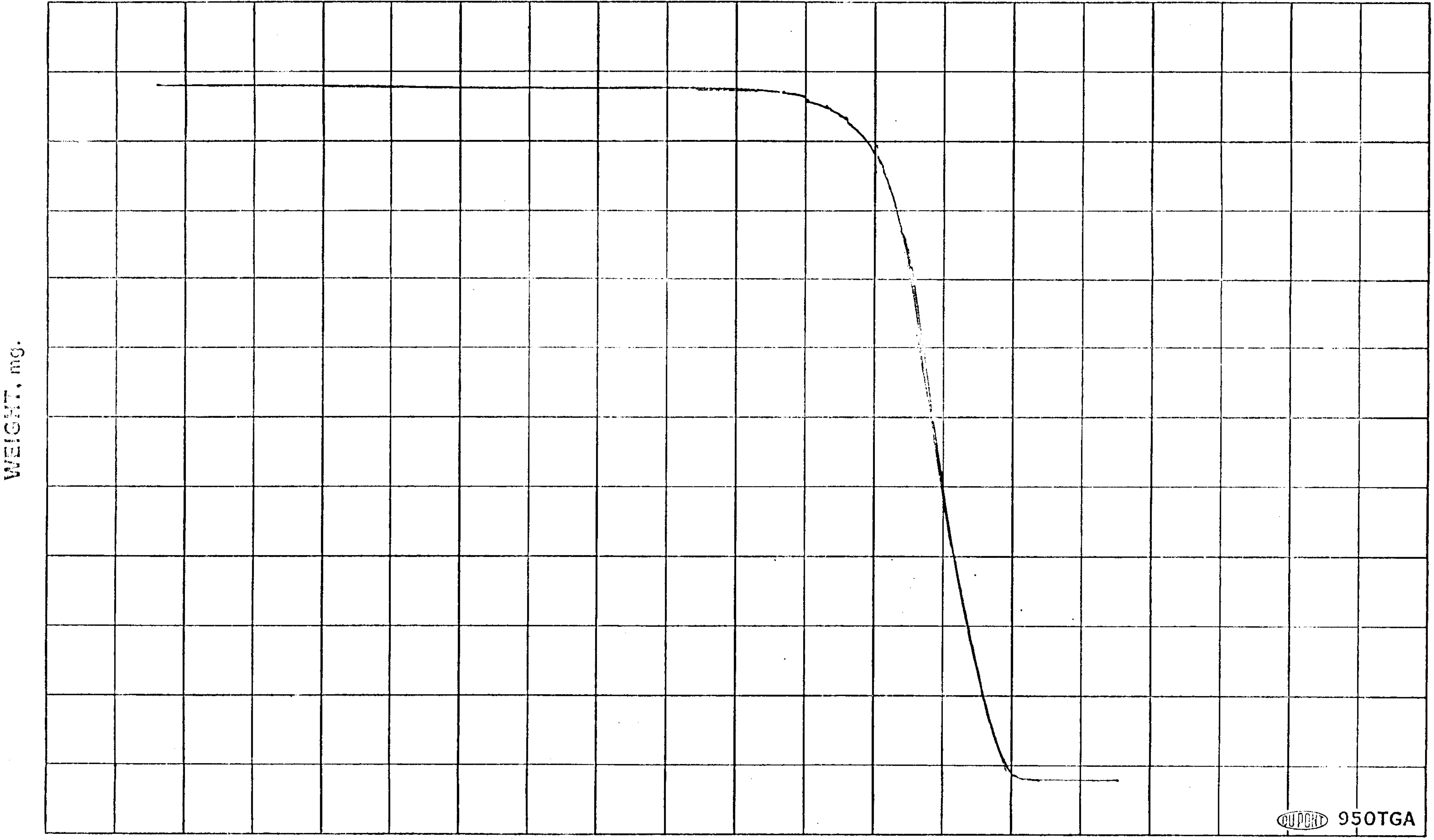


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 20

E. I. DU PONT DE NEMOURS & CO (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-37-18-H425 25 mole % m-$(H_2N)_2C_6H_4$ 75 mole % p-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent SIZE 10 mg.	**X-AXIS** TEMP. SCALE 100 °C/inch SHIFT 0 inch TIME SCALE (ALT.) 0	**Y-AXIS** SCALE 2 mg./inch (SCALE SETTING X 2) SUPPRESSION 0 mg.	RUN NO. DATE 7-27-65 OPERATOR TO HEATING RATE 15 °C/min. ATM. air TIME CONSTANT 2 sec.



TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

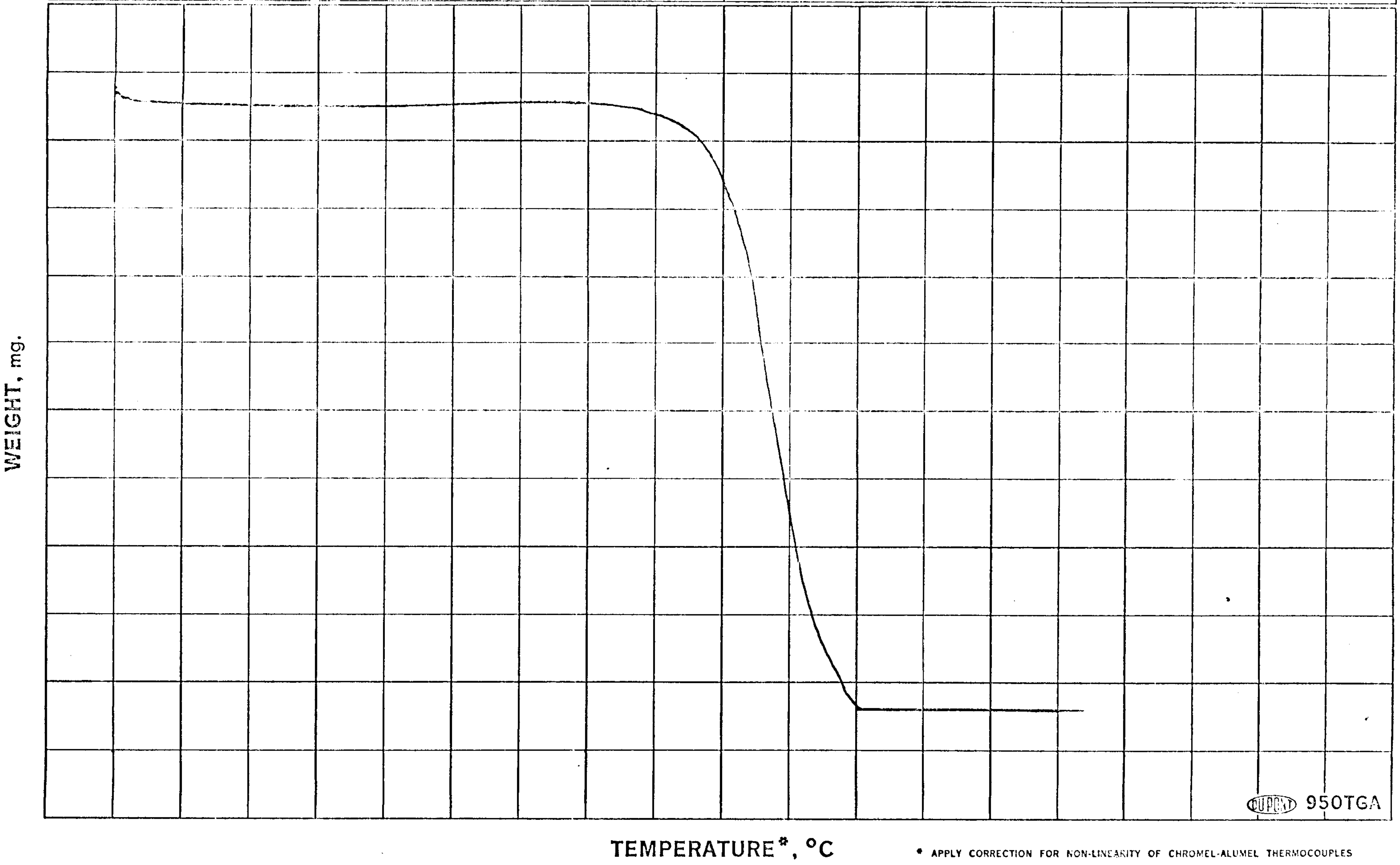
Appendix No. 21

SAMPLE: DA-37-18-H600
25 mole % m-$(H_2N)_2C_6H_4$
75 mole % p-$(H_2N)_2C_6H_4$
p-[$(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
SIZE 10 mg.

X-AXIS
TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. DATE 8-4-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 22

E. I. DU PONT DE NEMOURS & CO (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-19
p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
initial reflux

SIZE 10 mg.

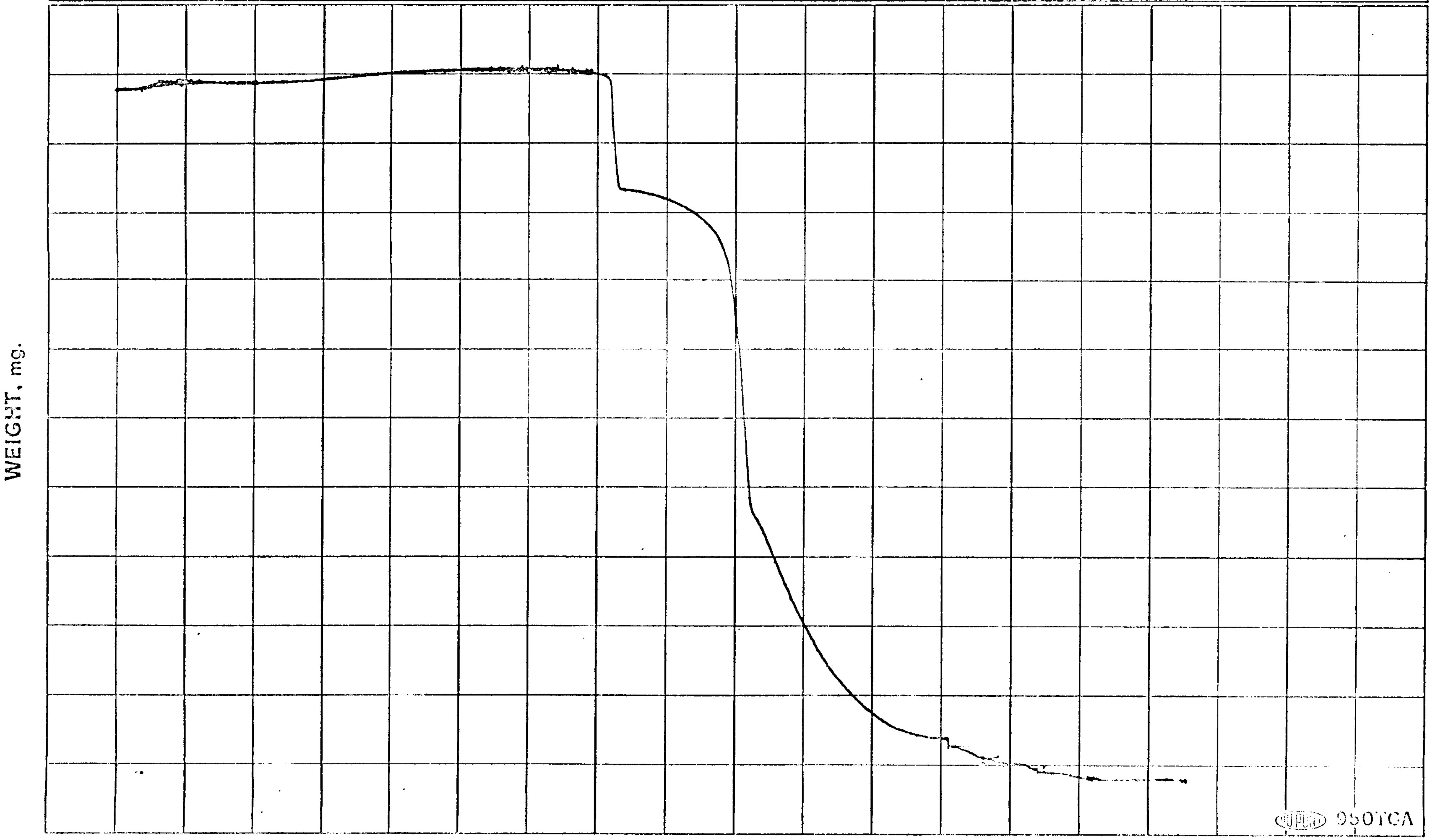
X-AXIS

TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS

SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. ______ DATE 7-25-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



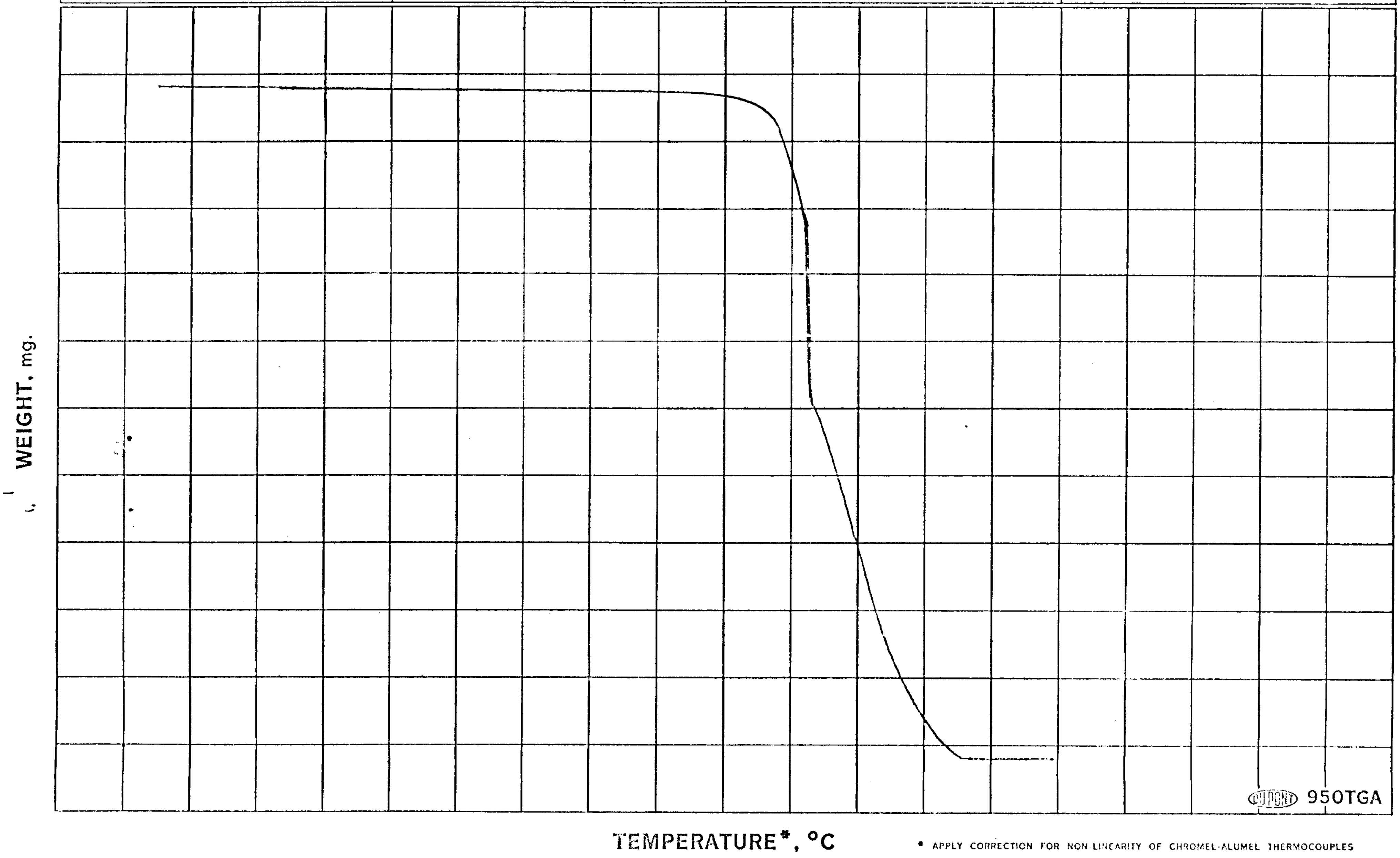
TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 23

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-19-H425 p-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent, initial reflux SIZE 10 mg.	**X-AXIS** TEMP. SCALE 100 °C/inch SHIFT 0 inch TIME SCALE (ALT.) 0	**Y-AXIS** SCALE 2 mg./inch (SCALE SETTING X 2) SUPPRESSION 0 mg.	RUN NO. DATE 7-27-65 OPERATOR TO HEATING RATE air °C/min. ATM. TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 24

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-37-19-H600
p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
initial reflux
SIZE 10 mg.

X-AXIS
TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO.
DATE 8-4-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-20
p-$(C_6H_5\text{-}CH{=}N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
$ZnCl_2$, no solvent

SIZE 10 mg.

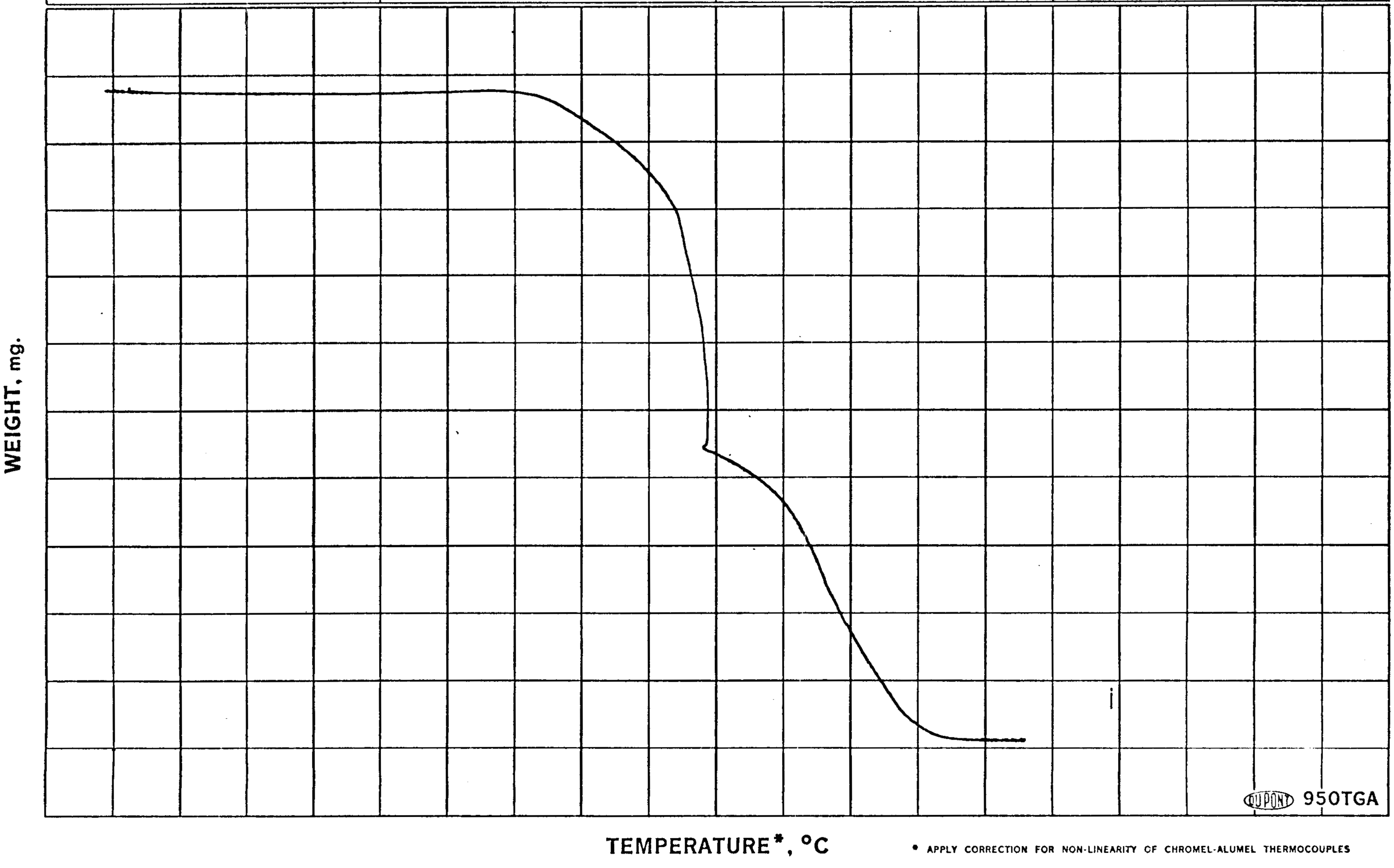
X-AXIS

TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS

SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. **DATE** 8-5-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 26

E. I. DU PONT DE NEMOURS & CO (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-37-20-H425
p-$(C_6H_5\text{-}CH{=}N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
$ZnCl_2$, no solvent

SIZE 10 mg.

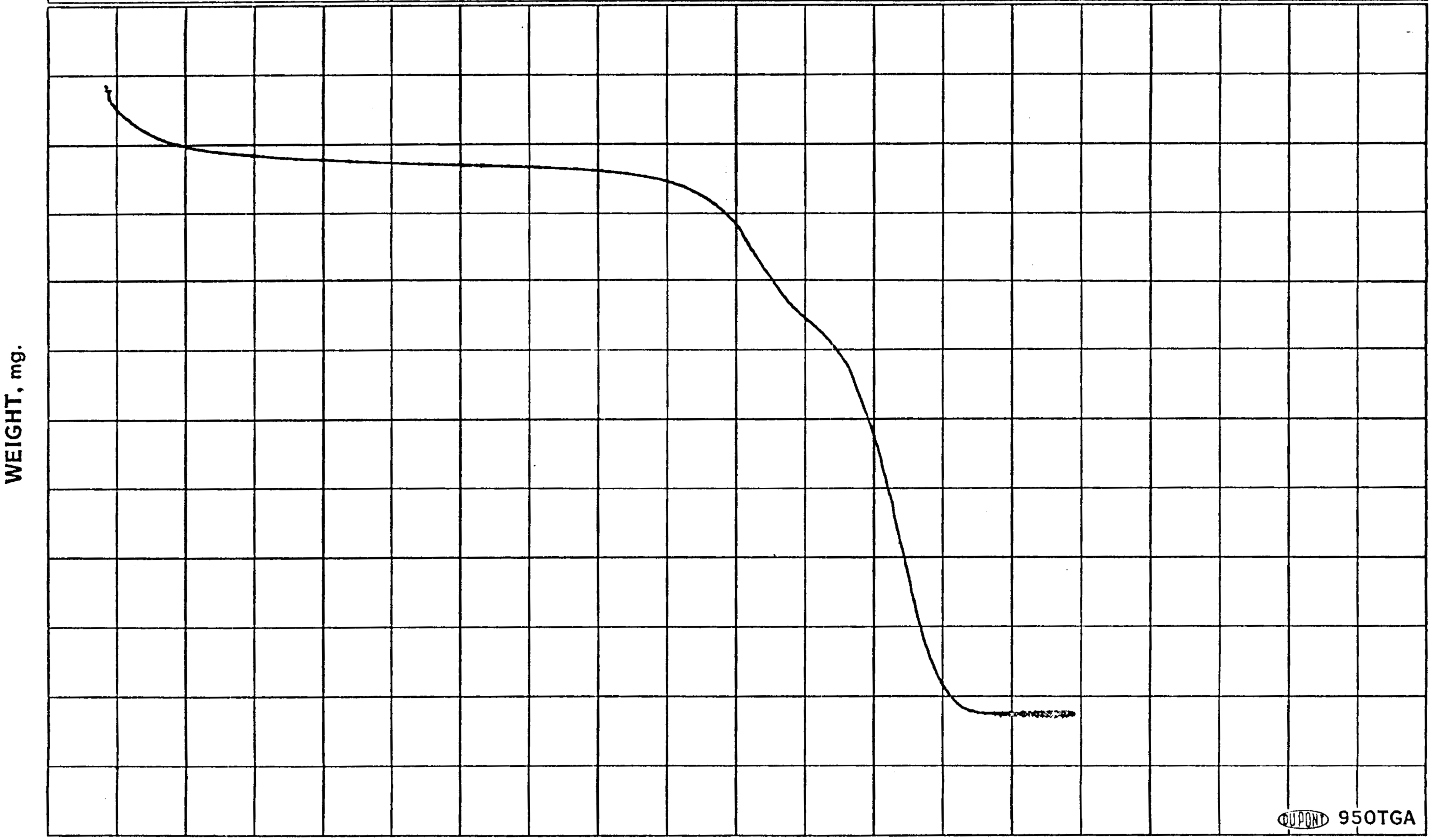
X-AXIS

TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS

SCALE 0 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

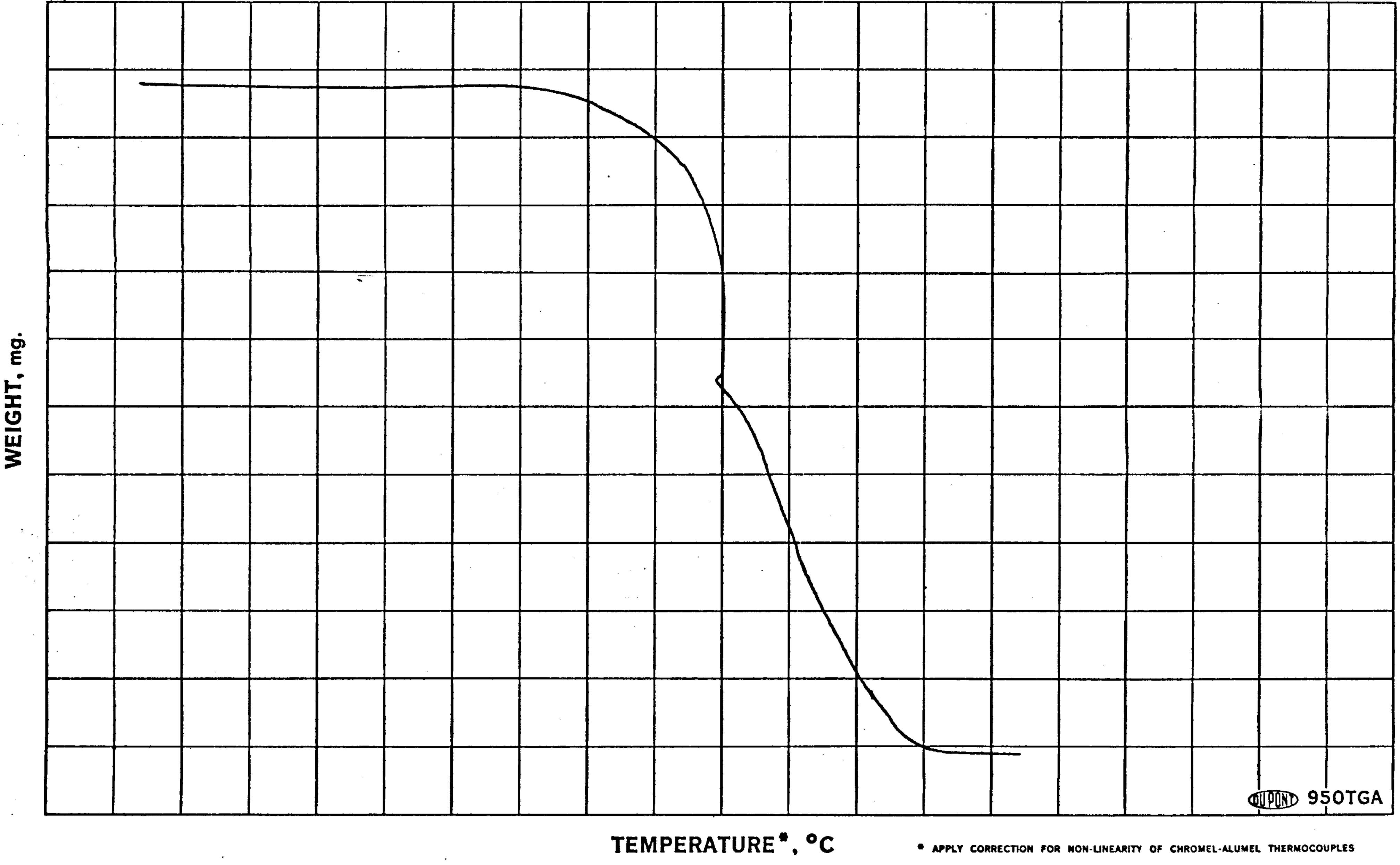
RUN NO. **DATE** 8-5-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

E I DU PONT DE NEMOURS & CO (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

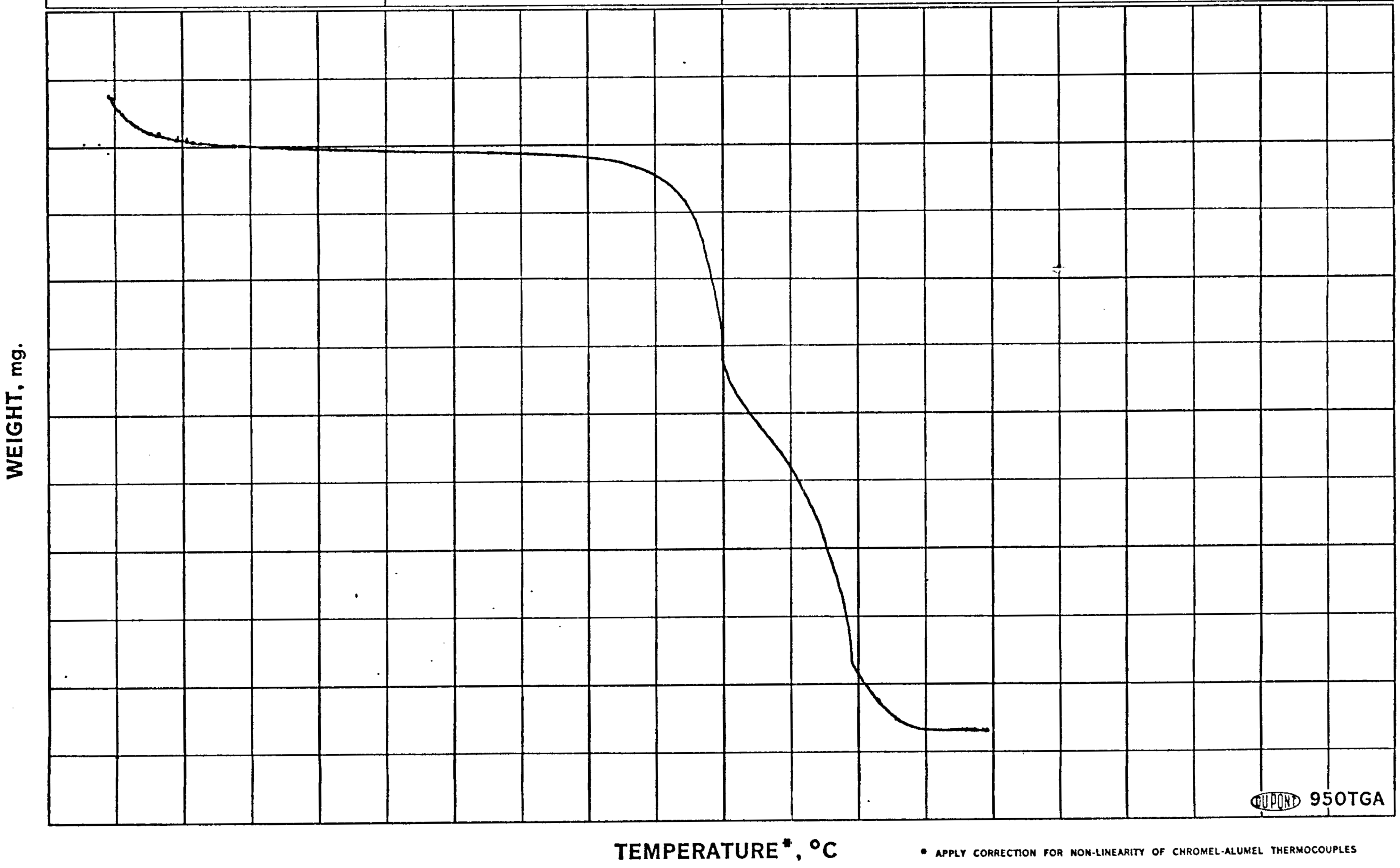
SAMPLE	X-AXIS	Y-AXIS	
SAMPLE: DA-37-21 p-$(C_6H_5\text{-}CH{=}N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ $C_6H_5N{=}CHC_6H_5$ $ZnCl_2$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	RUN NO. ____ DATE 8-5-65 OPERATOR TO HEATING RATE 15 °C/min. ATM. air
SIZE 10 mg.	SHIFT 0 inch TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-21-H425 p-$(C_6H_5\text{-}CH{=}N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ $C_6H_5N{=}CHC_6H_5$ $ZnCl_2$ SIZE 10 mg.	**X-AXIS** TEMP. SCALE 100 °C/inch SHIFT 0 inch TIME SCALE (ALT.) 0	**Y-AXIS** SCALE 2 mg./inch (SCALE SETTING X 2) SUPPRESSION 0 mg.	RUN NO. DATE 8-5-65 OPERATOR TO HEATING RATE 15 °C/min. ATM. air TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

E. I. DU PONT DE NEMOURS & CO (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-22
m-$(C_6H_5\text{-}CH{=}N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent

SIZE 10 mg.

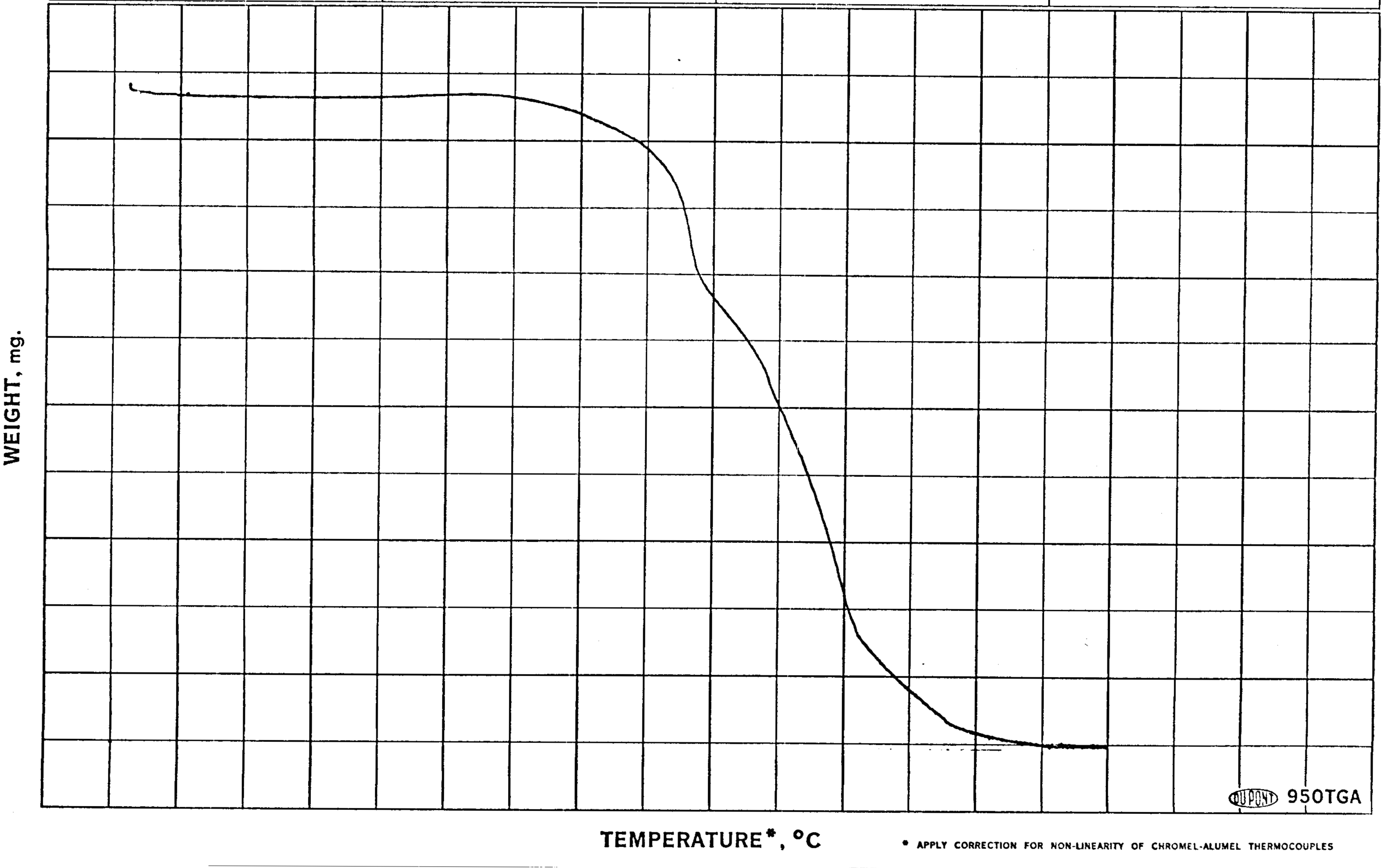
X-AXIS

TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS

SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. ______ DATE 7-4-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.

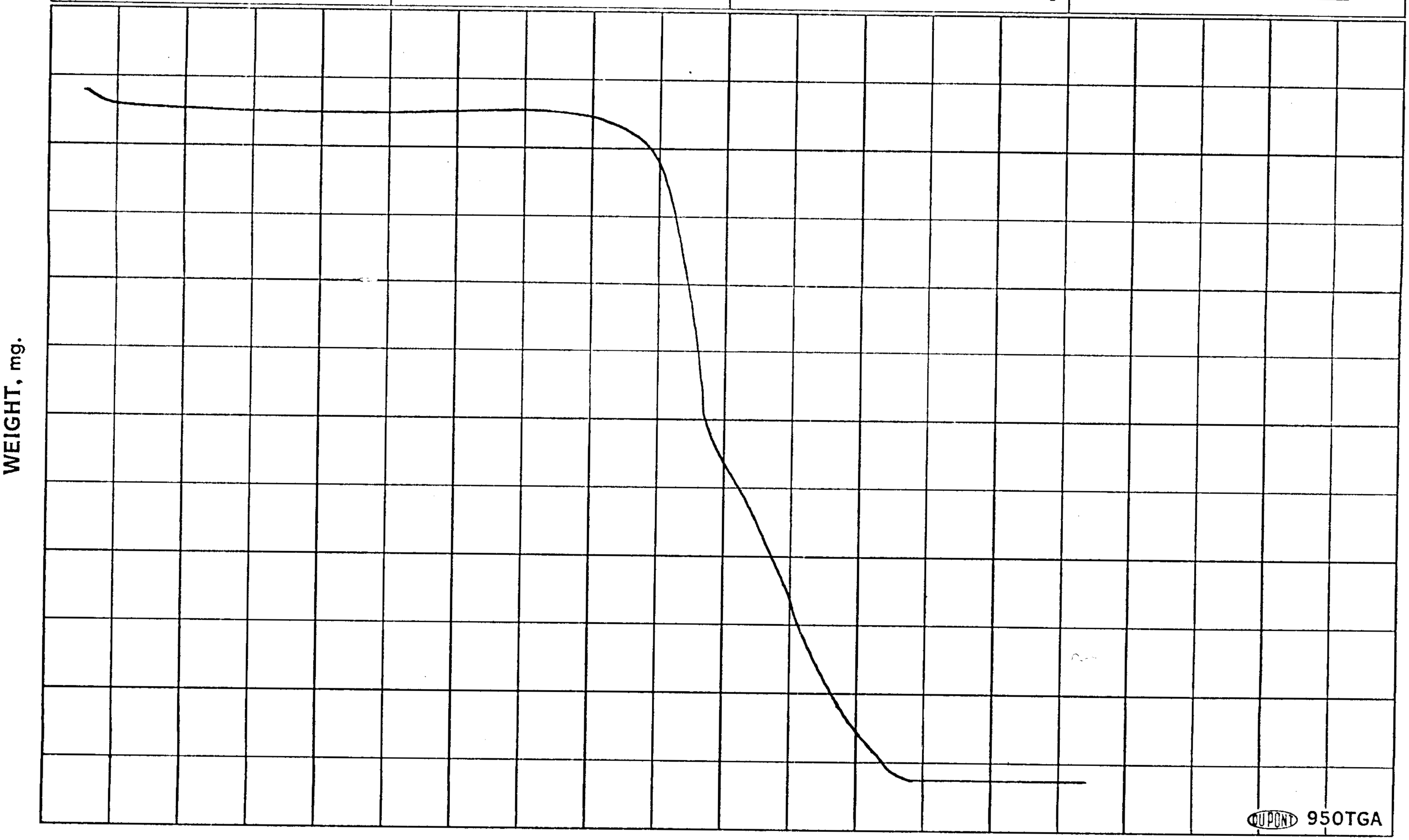


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 30

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-22-H425 m-$(C_6H_5-CH{=}N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent **SIZE** 10 mg.	**X-AXIS** **TEMP. SCALE** 100 °C/inch **SHIFT** 0 inch **TIME SCALE (ALT.)** 0	**Y-AXIS** **SCALE** 2 mg./inch (SCALE SETTING X 2) **SUPPRESSION** 0 mg.	**RUN NO.** **DATE** 7-4-65 **OPERATOR** TO **HEATING RATE** 15 °C/min. **ATM.** air **TIME CONSTANT** 2 sec.



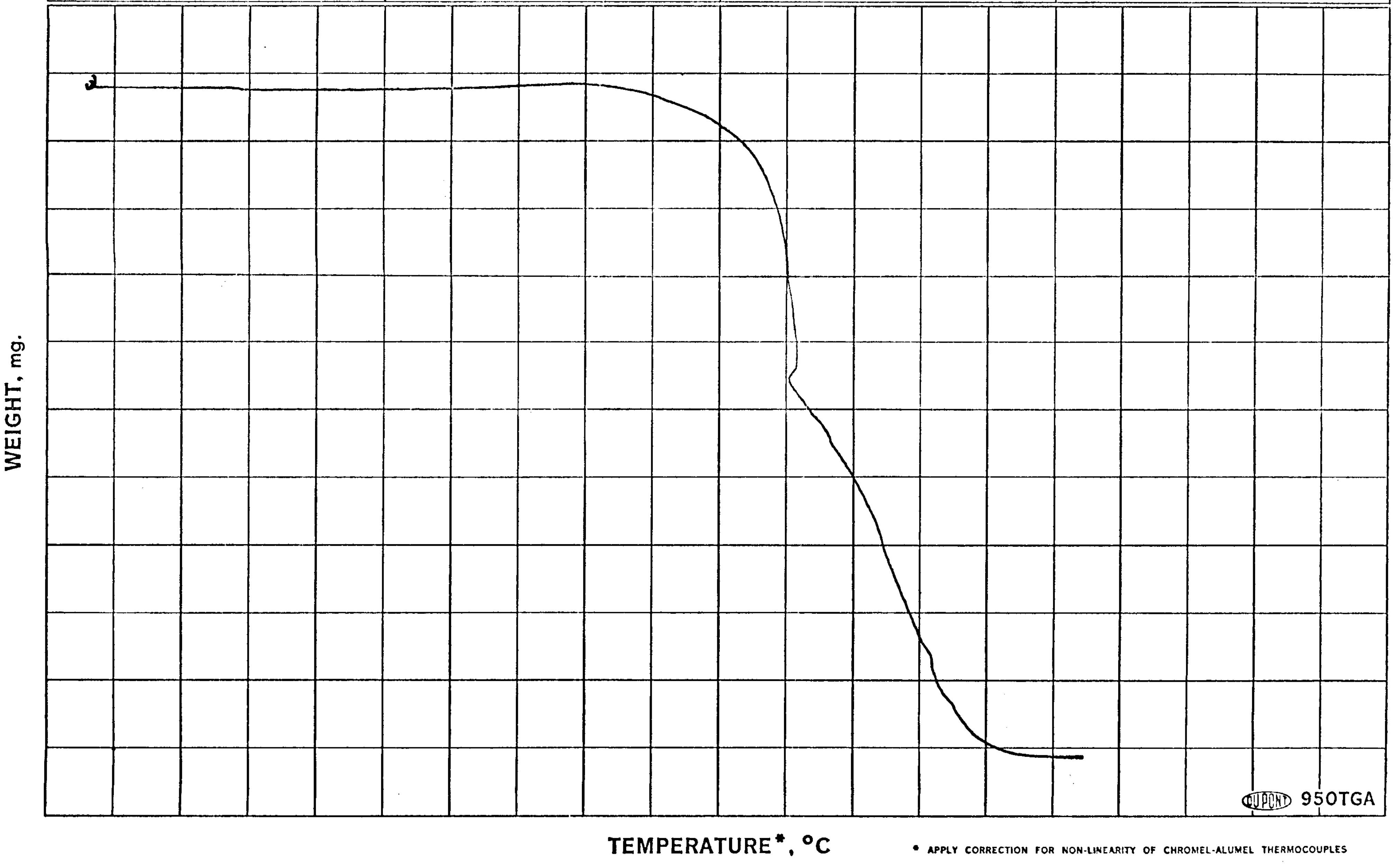
TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 31

DUPONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-37-23 m-$(C_6H_5\text{-}CH{=}N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ $C_6H_5N{=}CHC_6H_5$ $ZnCl_2$ SIZE 10 mg.	X-AXIS TEMP. SCALE 100 °C/inch SHIFT 0 inch TIME SCALE (ALT.) 0	Y-AXIS SCALE 2 mg./inch (SCALE SETTING X 2) SUPPRESSION 0 mg.	RUN NO. ____ DATE 8-5-65 OPERATOR TO HEATING RATE 15 °C/min. ATM. air TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-37-23-H425
m-$(C_6H_5-CH=N)_2C_6H_4$
$C_6H_5N=CHC_6H_5$
$ZnCl_2$

SIZE 10 mg.

X-AXIS

TEMP. SCALE 100 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 0 mg.

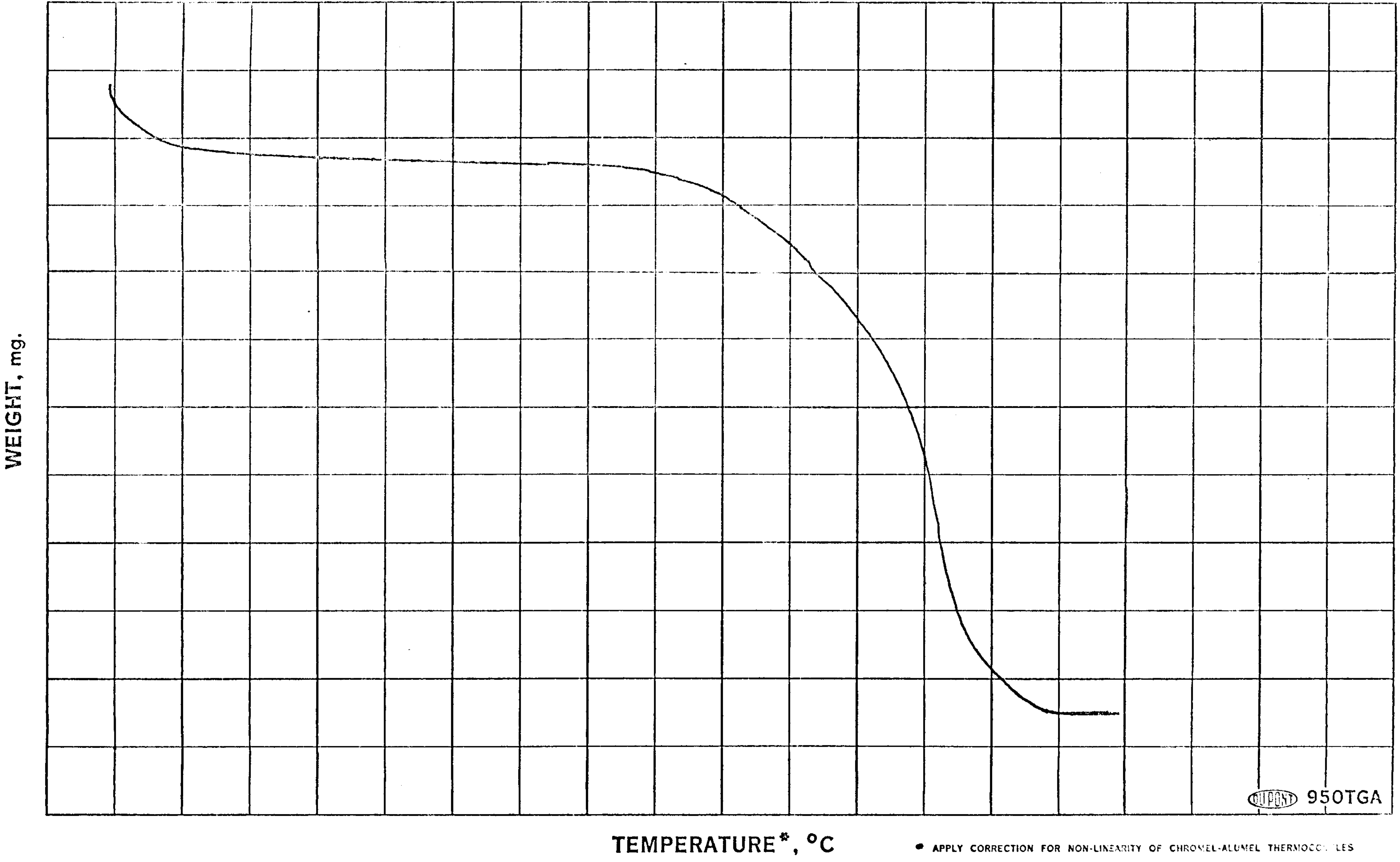
RUN NO. **DATE** 8-5-65

OPERATOR TO

HEATING RATE 15 °C/min.

ATM. air

TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-24
p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent

SIZE 10 mg.

X-AXIS

TEMP. SCALE 100 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS

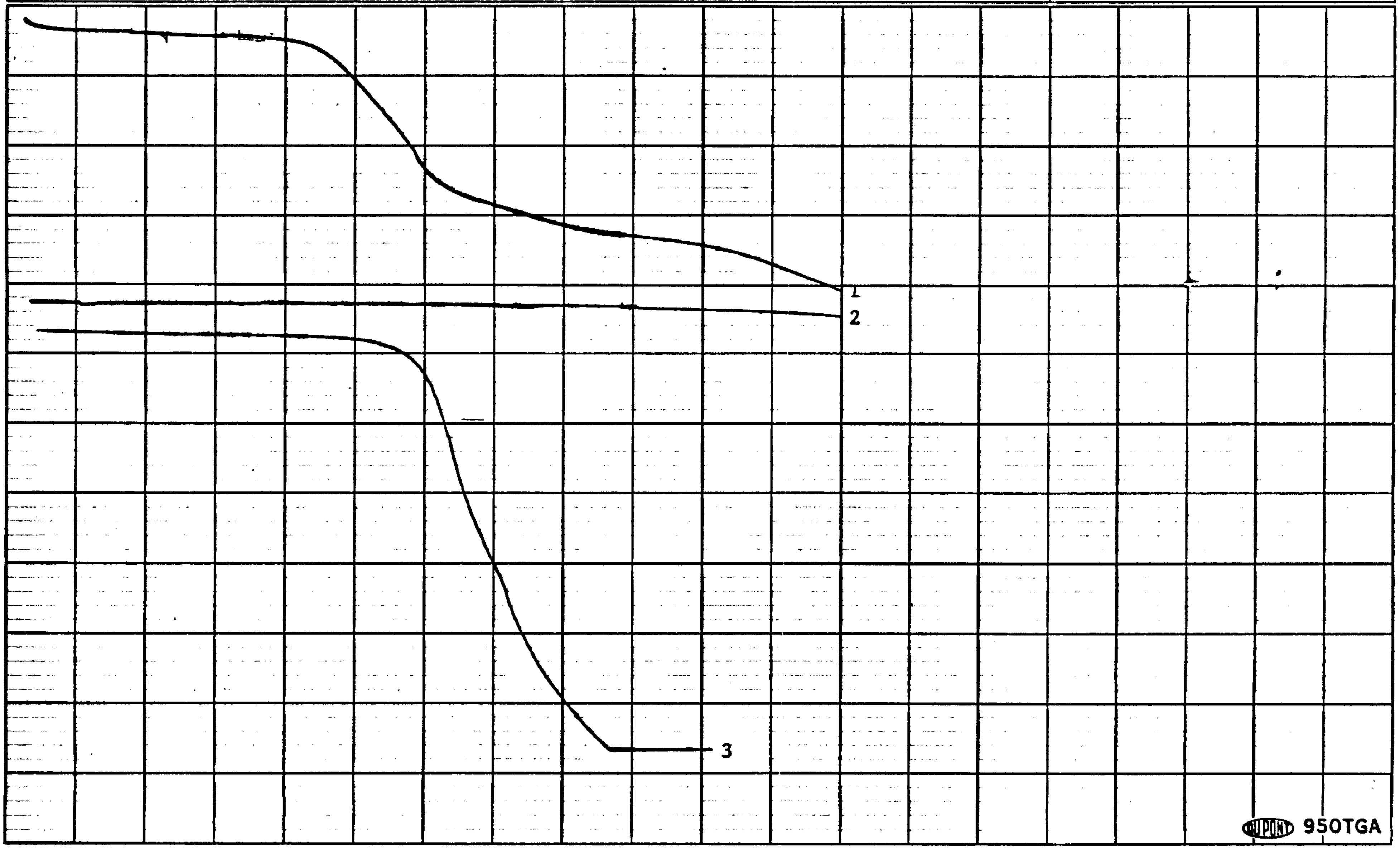
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. ______ DATE 8-11-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

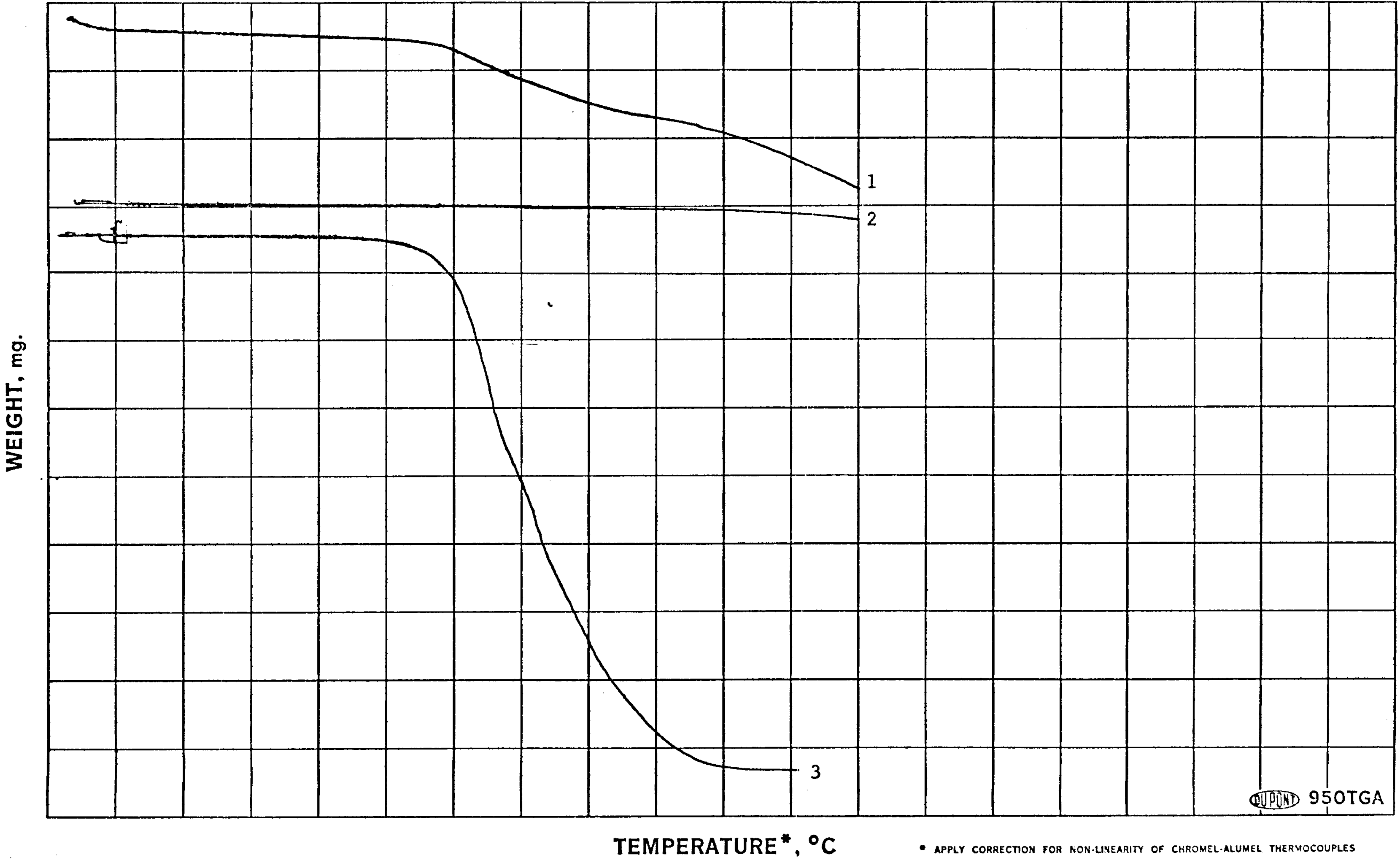
SAMPLE: DA-37-12 m-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ $C_6H_5N{=}CHC_6H_5$ SIZE 10 mg.	X-AXIS TEMP. SCALE 200 °C/inch SHIFT 0 inch TIME SCALE (ALT.) 0	Y-AXIS SCALE 2 mg./inch (SCALE SETTING X 2) SUPPRESSION 0 mg.	RUN NO. DATE 8-8-65 OPERATOR TO HEATING RATE 15 °C/min. ATM. 1) N_2, 2) rerun in N_2, 3) air TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

E. I. DU PONT DE NEMOURS & CO (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-37-12-H425 m-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ $C_6H_5N{=}CHC_6H_5$	**X-AXIS**	**Y-AXIS**	RUN NO. ____ DATE 8-5-65
	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR TO
	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. 1) N_2, 2) rerun in N_2, 3) air
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-12-H600
m-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
$C_6H_5N{=}CHC_6H_5$

SIZE 10 mg.

X-AXIS

TEMP. SCALE 200 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 0 mg.

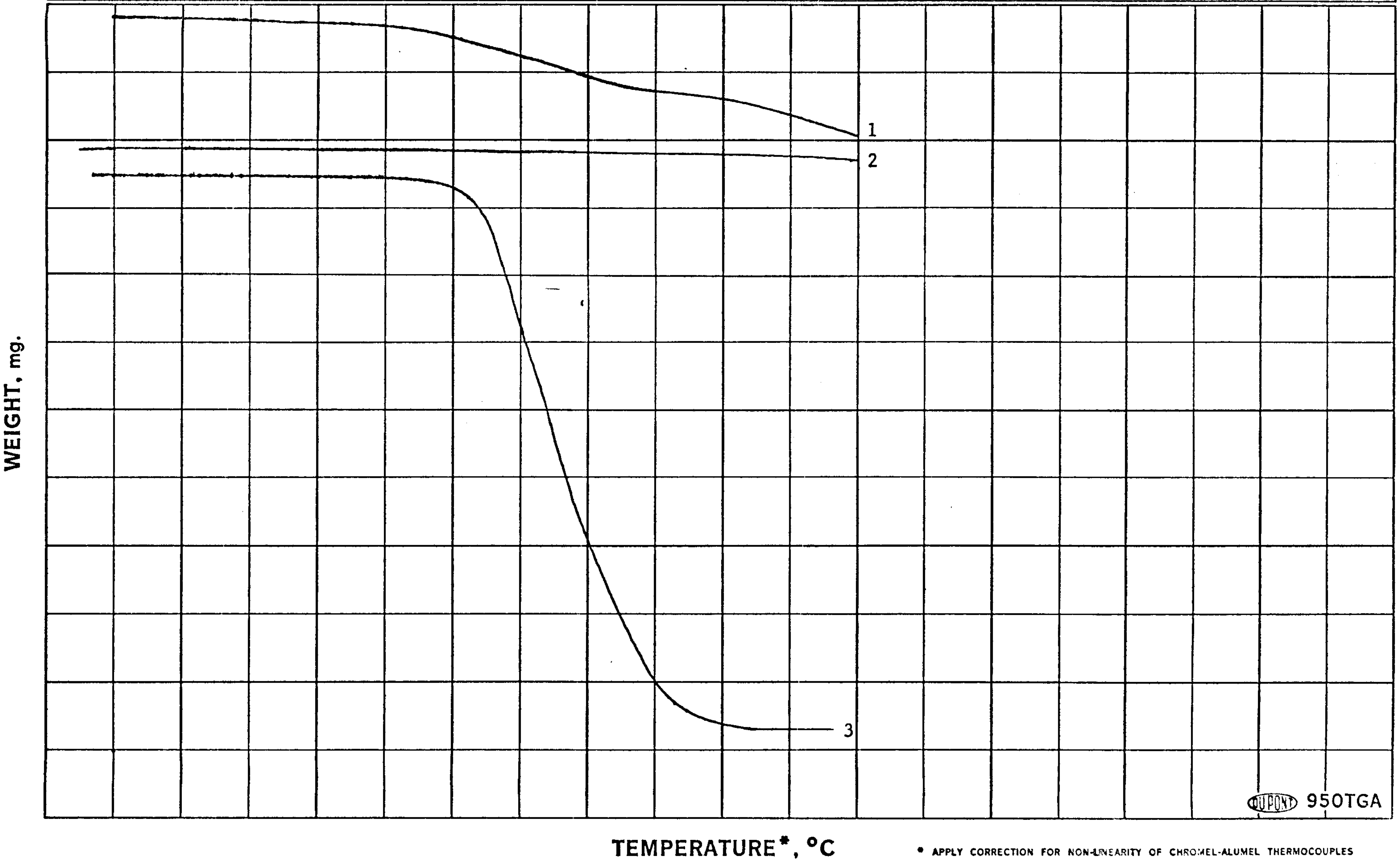
RUN NO. **DATE** 8-8-65

OPERATOR TO

HEATING RATE 15 °C/min.

ATM. 1) N_2, 2) rerun in N_2
3) air

TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-37-13
m-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent

SIZE 10 mg.

X-AXIS

TEMP. SCALE 200 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

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

SUPPRESSION 0 mg.

RUN NO.

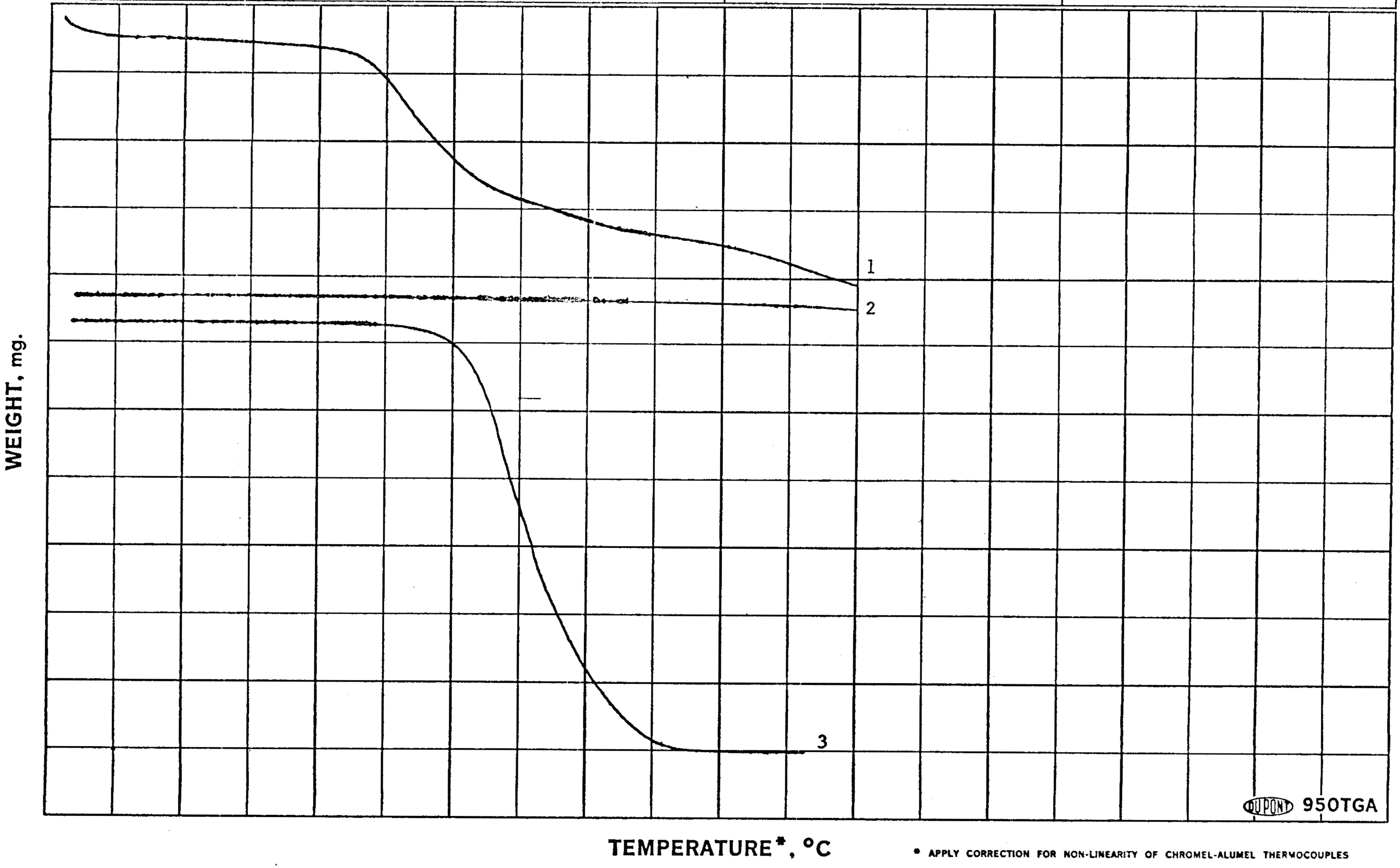
DATE 8-9-65

OPERATOR TO

HEATING RATE 15 °C/min.

ATM. 1) N_2, 2) rerun in N_2, 3) air

TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 38

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-13-H425
m-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent

SIZE 10 mg.

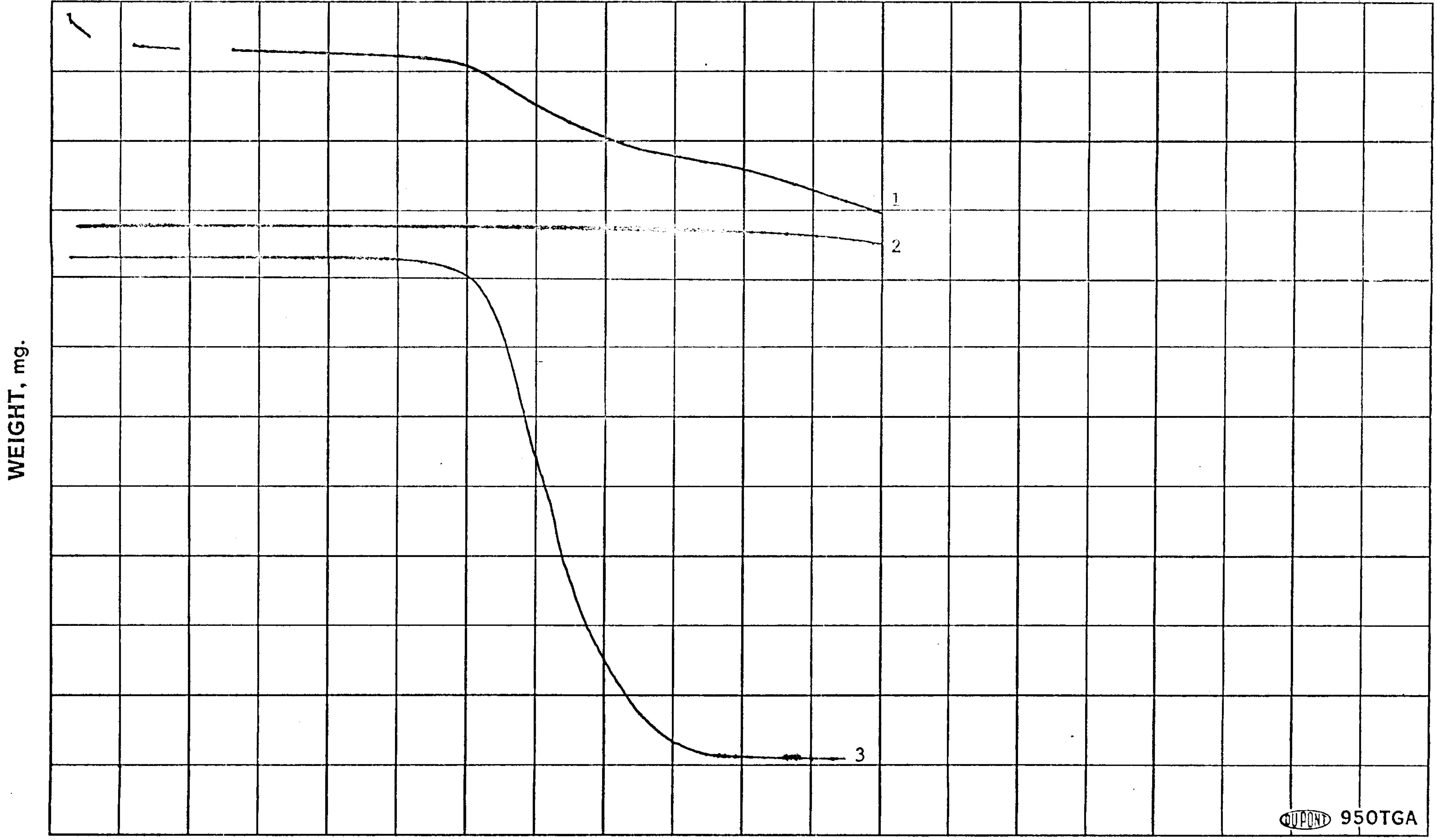
X-AXIS

TEMP. SCALE 200 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS

SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. ____ DATE 8-9-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. 1) N_2, 2) rerun in N_2 3) air
TIME CONSTANT 2 sec.



TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-37-13-H600
m-$(H_2N)_2C_6H_4$
p-[(n-BuO)$_2$CH]$_2C_6H_4$
no solvent

SIZE 10 mg.

X-AXIS

TEMP. SCALE 200 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

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

SUPPRESSION 0 mg.

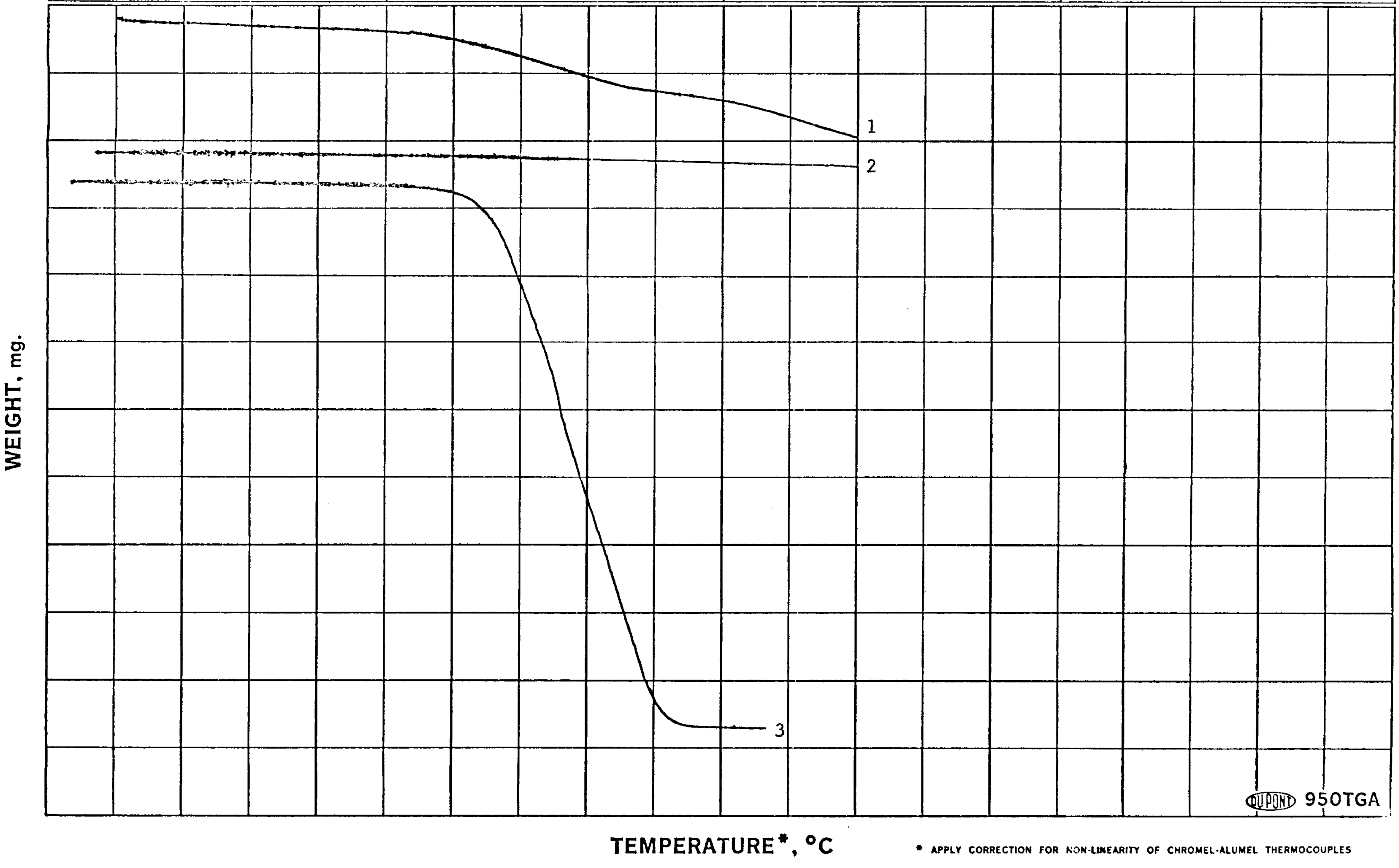
RUN NO. ______ **DATE** 8-9-65

OPERATOR TO

HEATING RATE 15 °C/min.

ATM. 1) N_2, 2) rerun in N_2, 3) air

TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

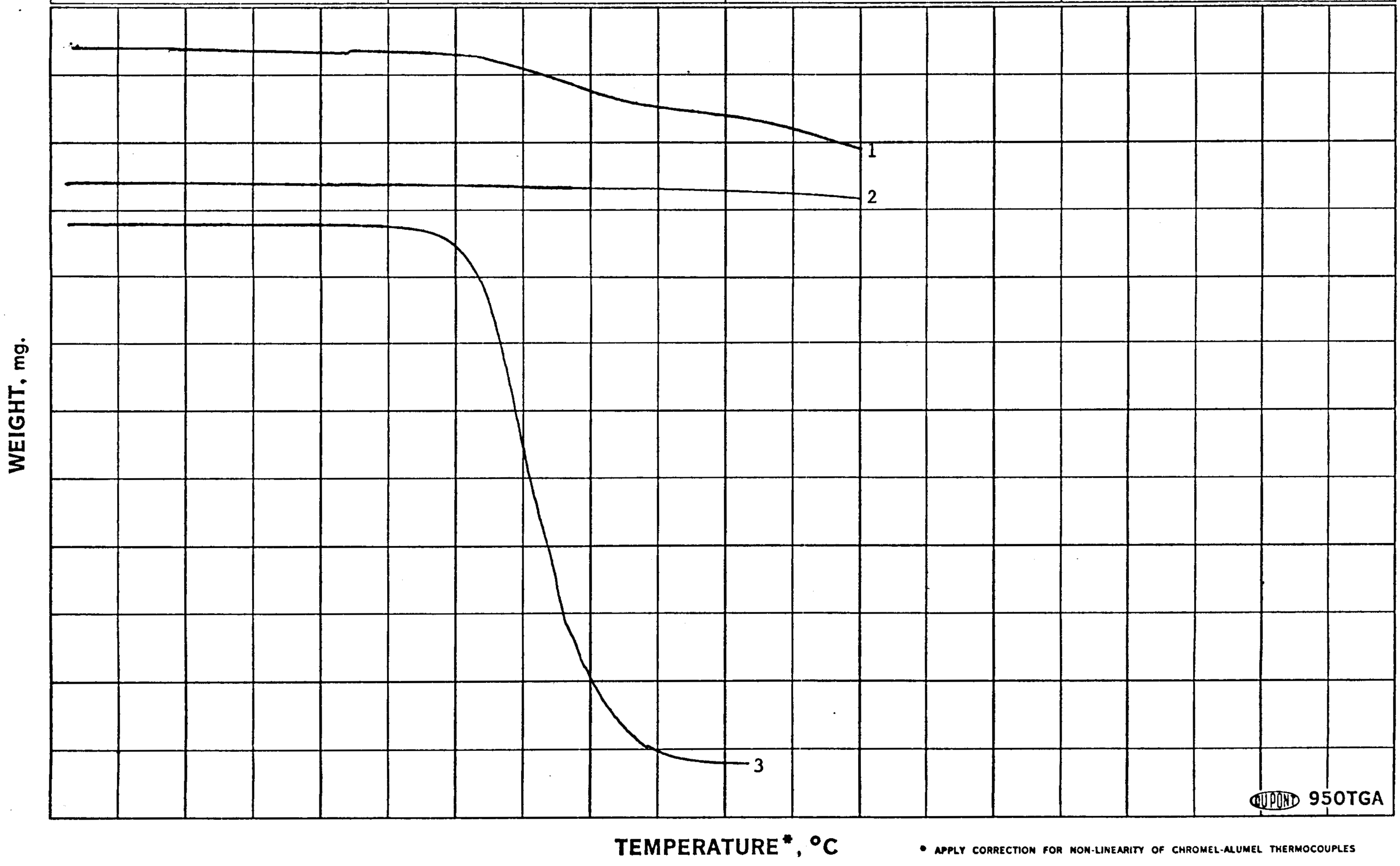
E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON DELAWARE

SAMPLE: DA-37-14-H600
50 mole % m-$(H_2N)_2C_6H_4$
50 mole % p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
SIZE 10 mg.

X-AXIS
TEMP. SCALE 200 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO.
DATE 9-3-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. 1) N_2, 2) rerun in N_2, 3) air
TIME CONSTANT 2 sec.

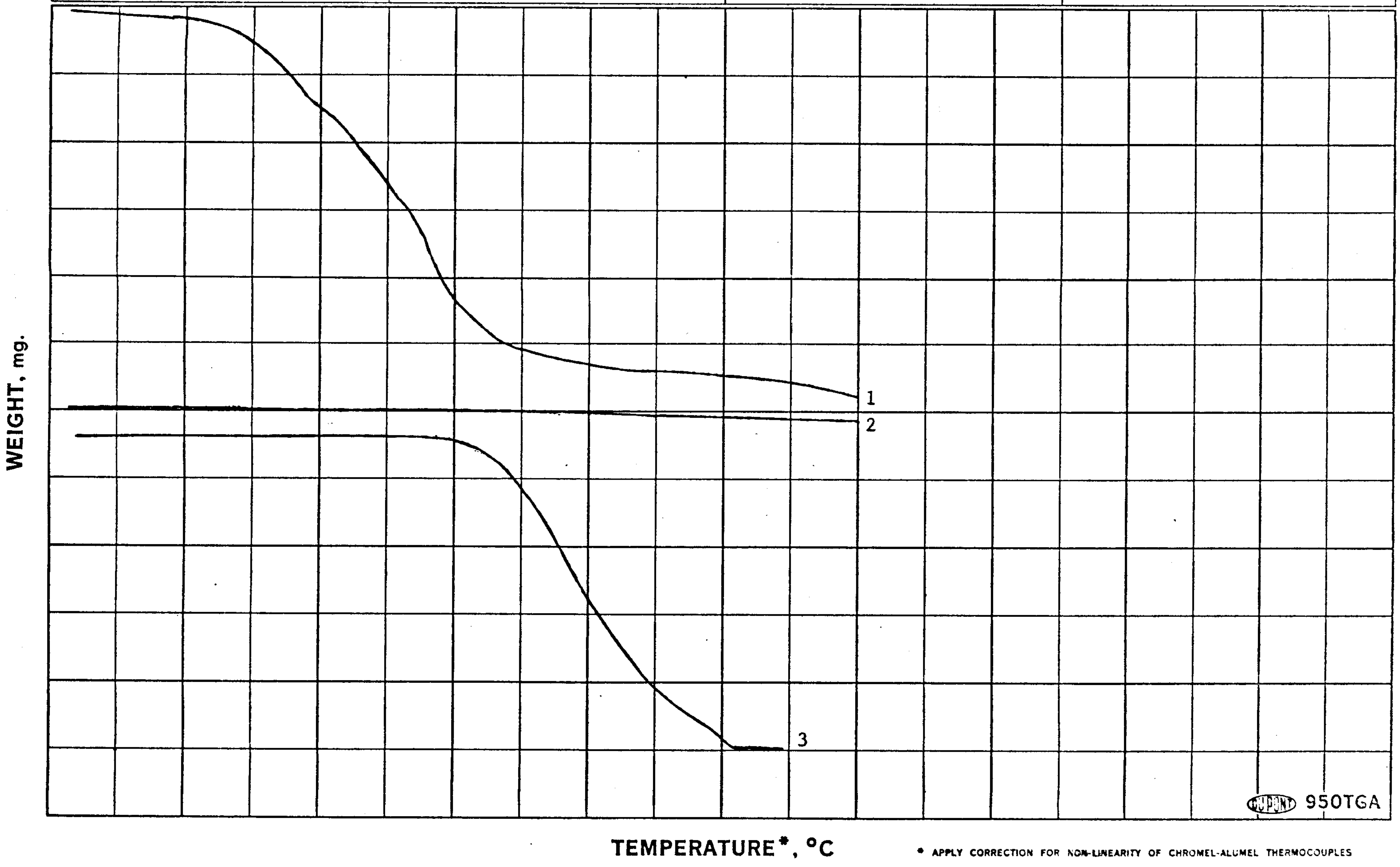


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 41

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE	X-AXIS	Y-AXIS	
SAMPLE: DA-37-15	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch	RUN NO. ____ DATE 8-10-65
p-$(H_2N)_2C_6H_4$	SHIFT 0 inch	(SCALE SETTING X 2)	OPERATOR TO
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	HEATING RATE 15 °C/min.
$C_6H_5N{=}CHC_6H_5$			ATM. 1) N_2, 2) rerun in N_2, 3) air
SIZE 10 mg.			TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-37-15-H425
$p\text{-}(H_2N)_2C_6H_4$
$p\text{-}[(n\text{-}BuO)_2CH]_2C_6H_4$
$C_6H_5N{=}CHC_6H_5$

SIZE 10 mg.

X-AXIS

TEMP. SCALE 200 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

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

SUPPRESSION 0 mg.

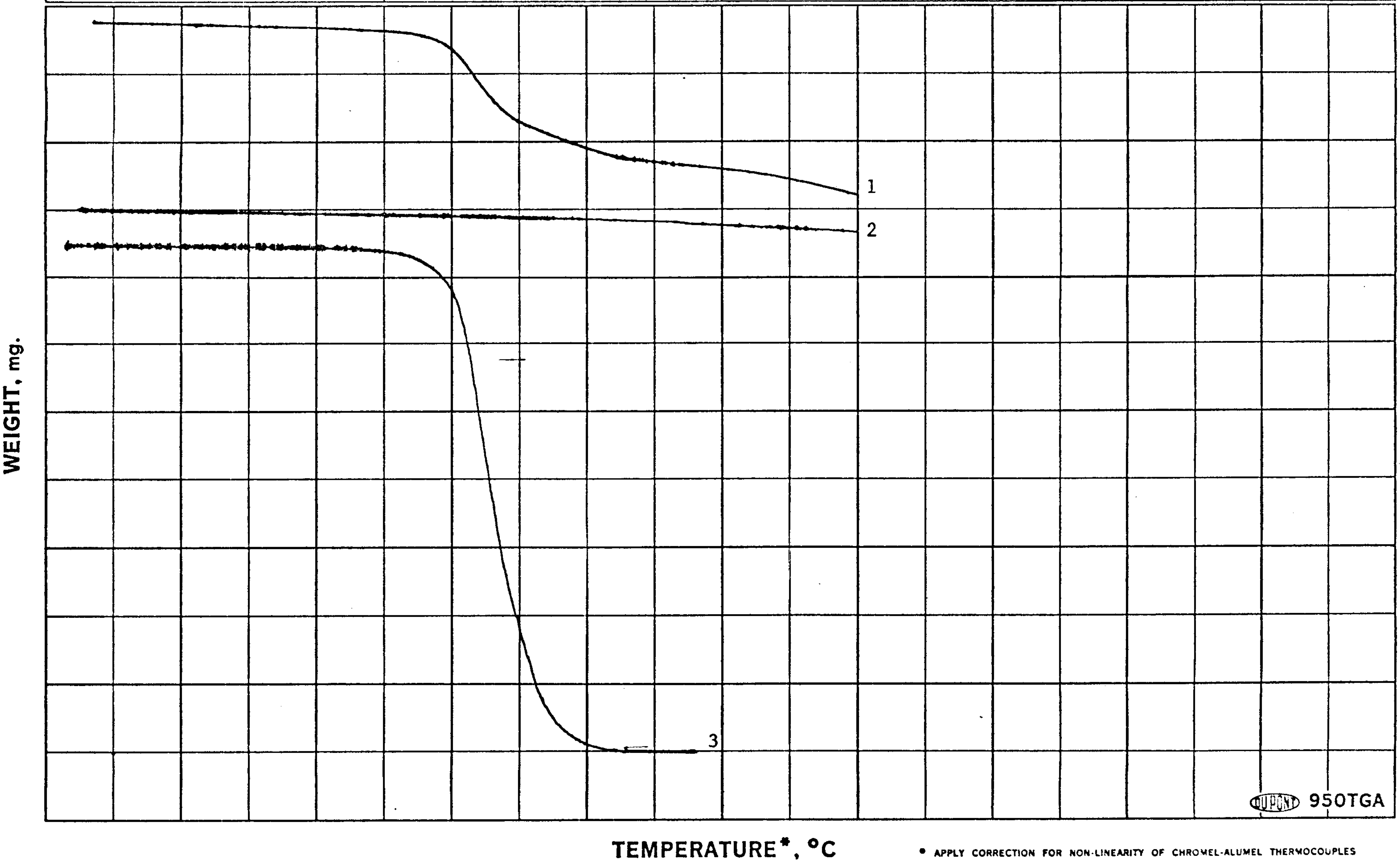
RUN NO. **DATE** 8-9-65

OPERATOR TO

HEATING RATE 15 °C/min.

ATM. 1) N_2, 2) rerun in N_2, 3) air

TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-15-H600
$p-(H_2N)_2C_6H_4$
$p-[(n-BuO)_2CH]_2C_6H_4$
$C_6H_5N=CHC_6H_5$

SIZE 10 mg.

X-AXIS

TEMP. SCALE 200 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 0 mg.

RUN NO.

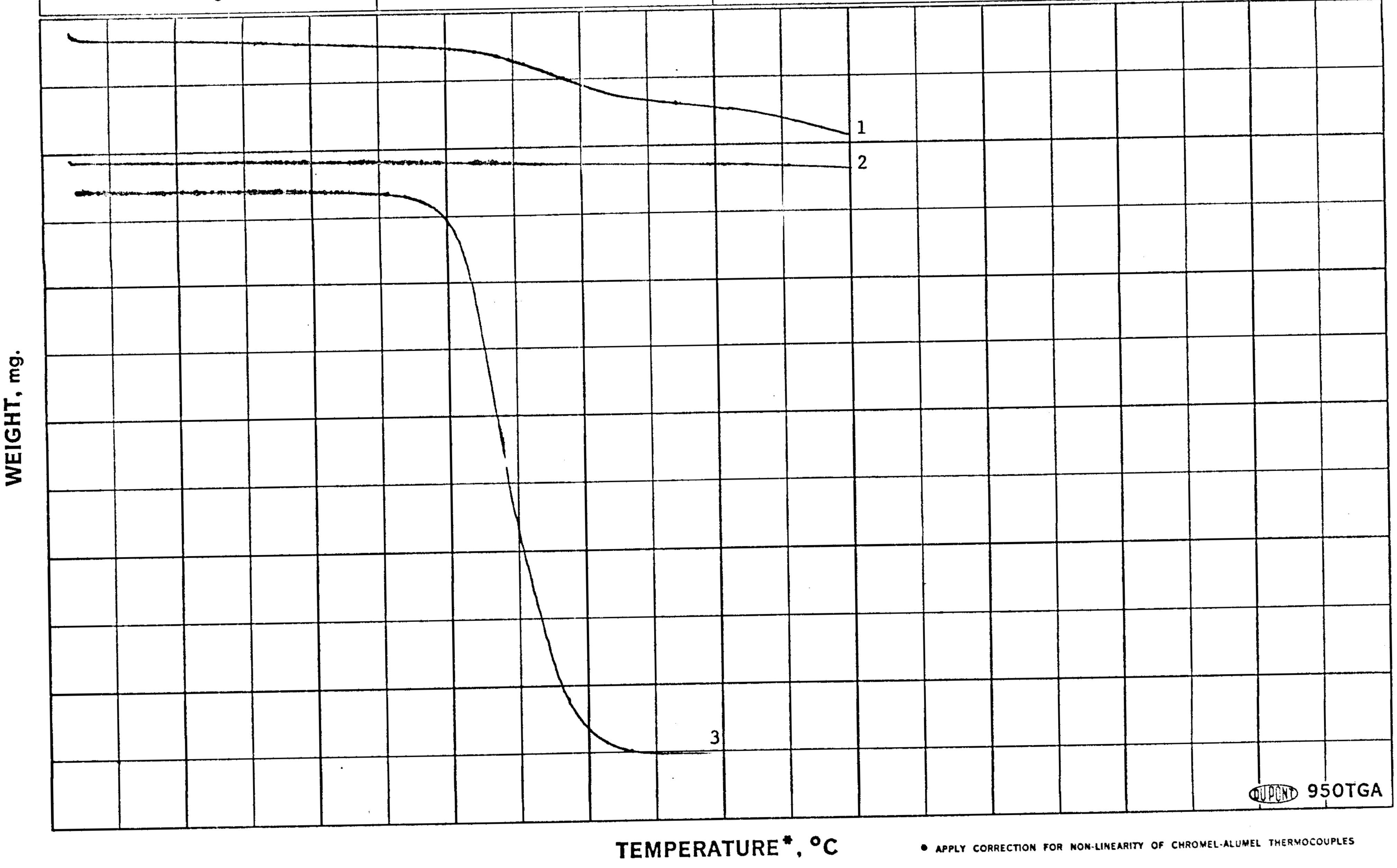
DATE 8-10-65

OPERATOR TO

HEATING RATE 15 °C/min.

ATM. 1) N_2, 2) rerun in N_2, 3) air

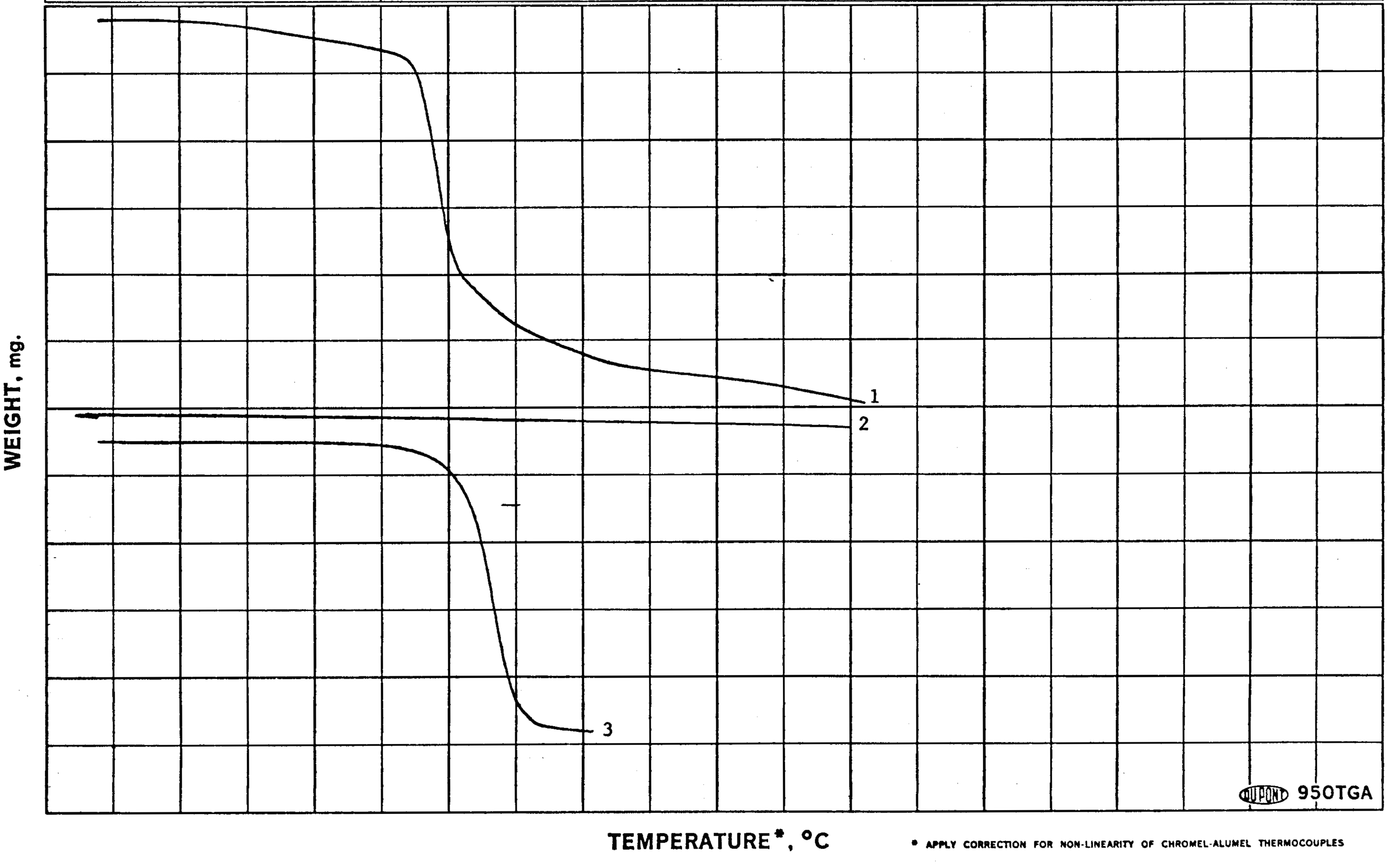
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DUPONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-16 p-$(H_2N)_2C_6H_4$ p-[$(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent	**X-AXIS**	**Y-AXIS**	**RUN NO.** ____ **DATE** 8-11-65
	TEMP. SCALE 200 °C/inch	**SCALE** 2 mg./inch (SCALE SETTING X 2)	**OPERATOR** TO
	SHIFT 0 inch		**HEATING RATE** 15 °C/min.
			ATM. 1) N_2, 2) rerun in N_2, 3)
SIZE 10 mg.	**TIME SCALE (ALT.)** 0	**SUPPRESSION** 0 mg.	**TIME CONSTANT** 2 sec.

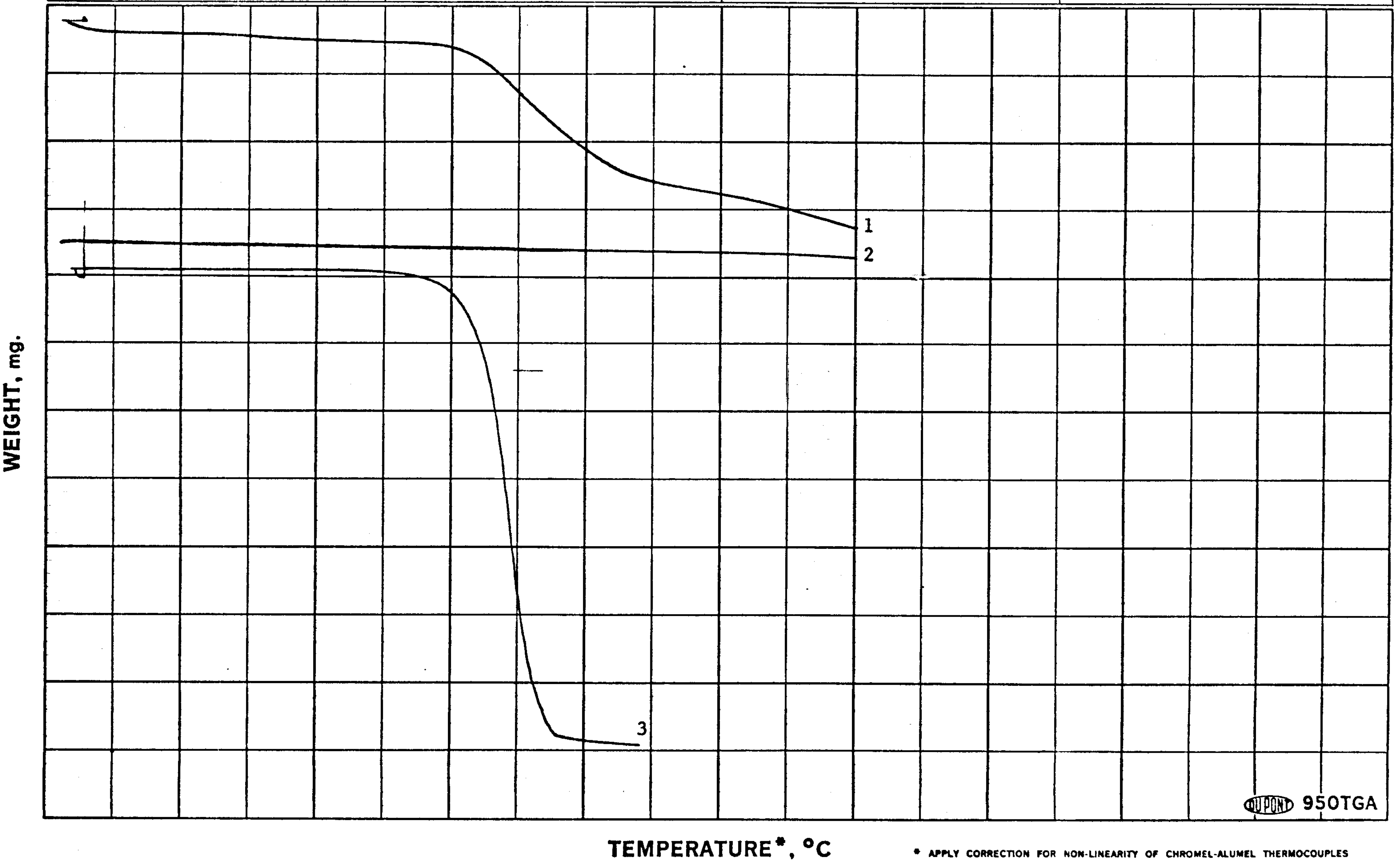


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 45

E I DU PONT DE NEMOURS & CO (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-16-H425 p-$(H_2N)_2C_6H_4$ p-$[(n\text{-}BuO)_2CH]_2C_6H_4$ no solvent	X-AXIS	Y-AXIS	RUN NO. ______ DATE 8-11-65
	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR TO
	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. 1) N_2, 2) rerun in N_2, 3) air
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

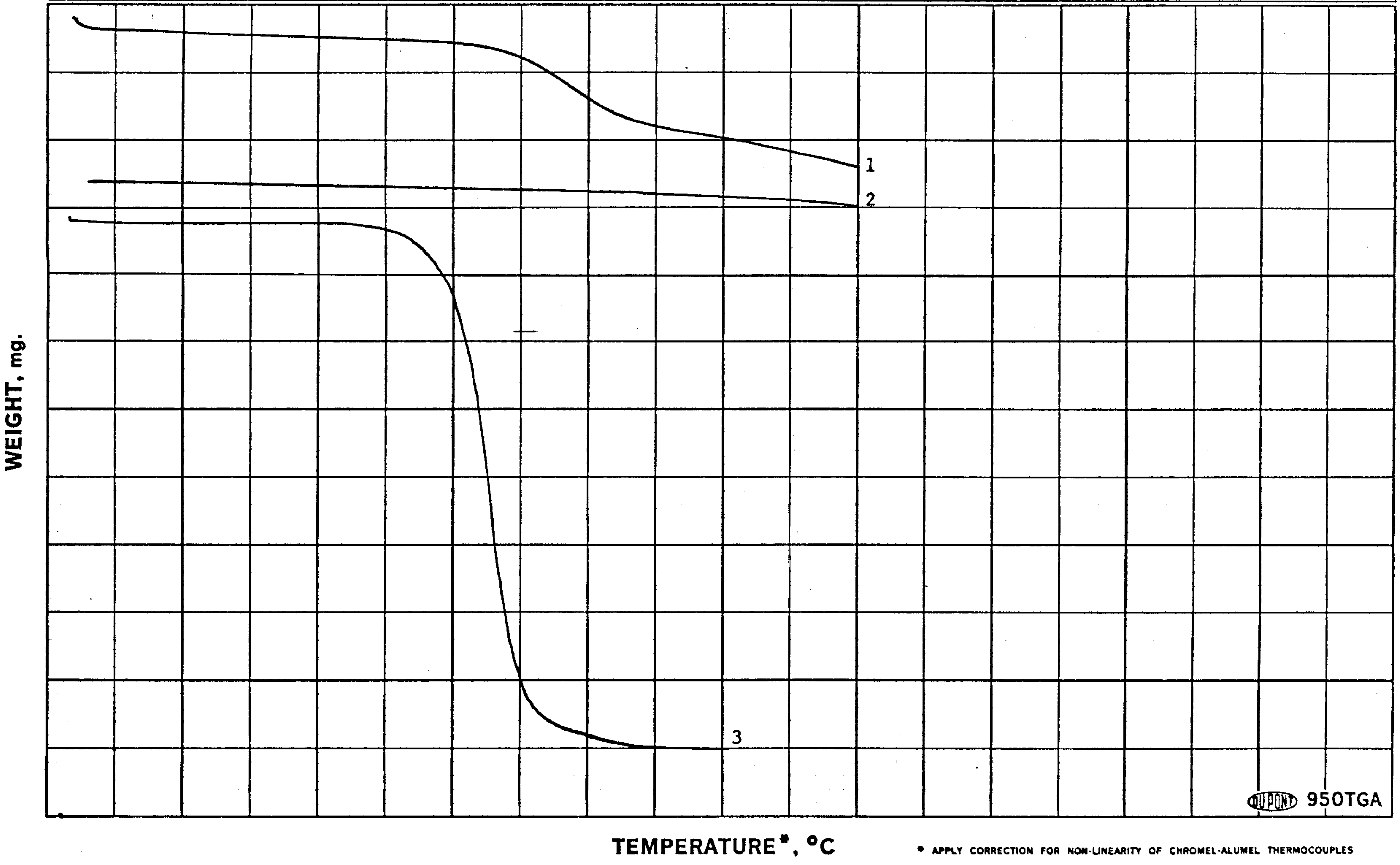
DUPONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-37-16-H600
p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
SIZE 10 mg.

X-AXIS
TEMP. SCALE 200 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO.
DATE 8-12-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. 1) N_2, 2) rerun in N_2, 3) air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 47

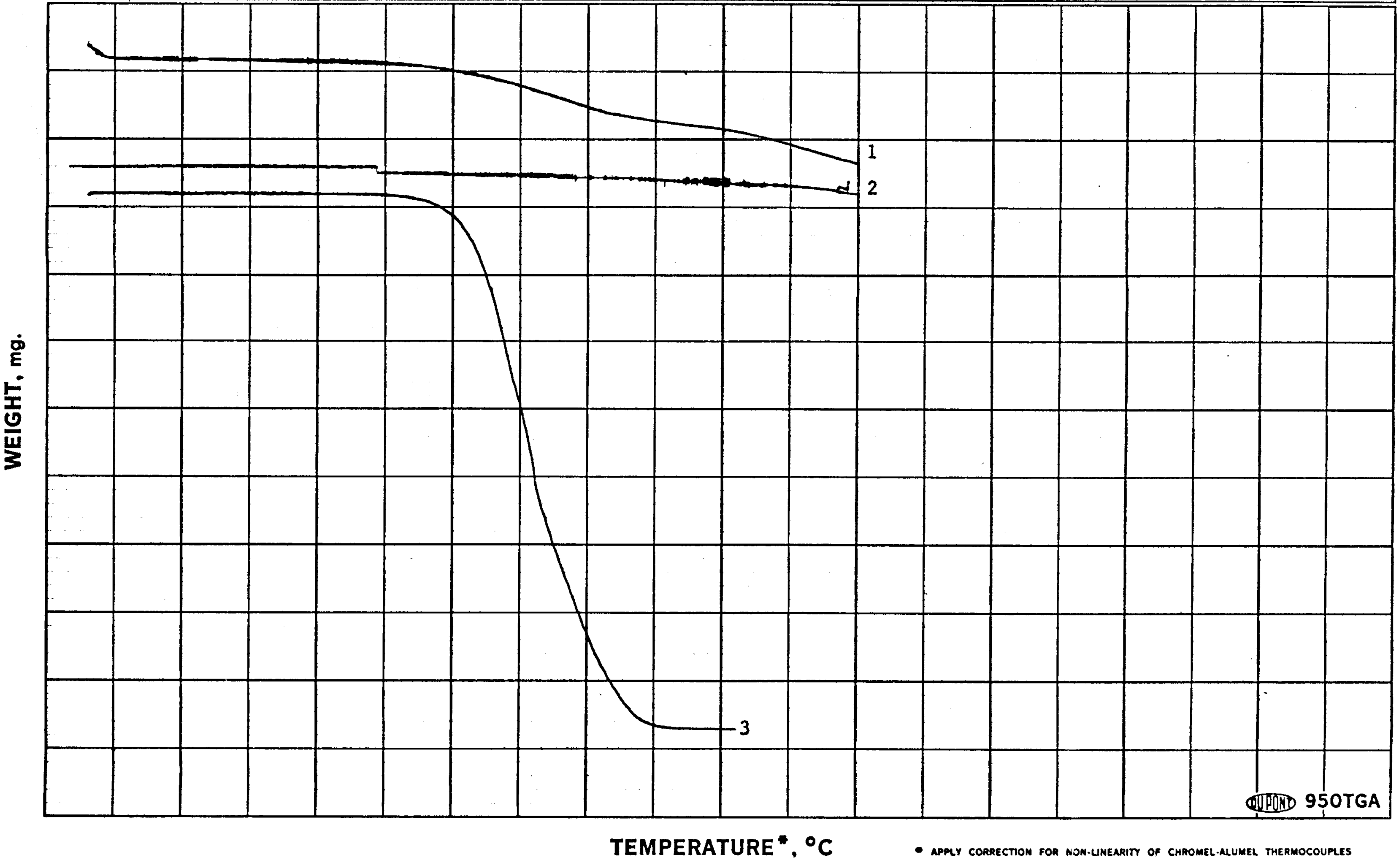
DUPONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-37-17-H600
25 mole % p-$(H_2N)_2C_6H_4$
75 mole % m-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
SIZE 10 mg.

X-AXIS
TEMP. SCALE 200 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO.
DATE 9-23-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. 1) N_2, 2) rerun in N_2, 3) air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 48

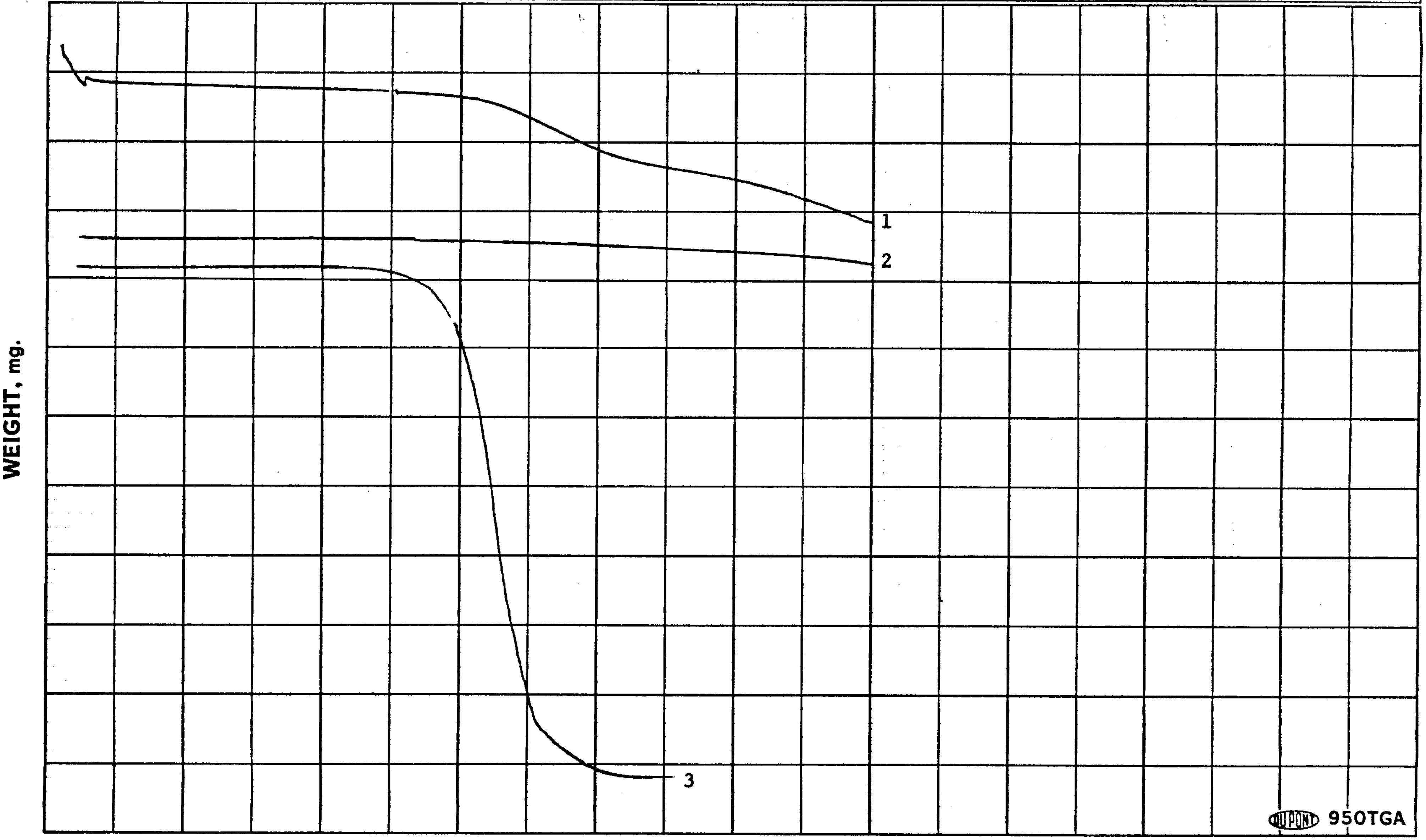
DUPONT | **INSTRUMENT PRODUCTS DIVISION**
WILMINGTON 98 DELAWARE

SAMPLE: DA-37-18-H600
25 mole % m-$(H_2N)_2C_6H_4$
75 mole % p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
SIZE 10 mg.

X-AXIS
TEMP. SCALE 200 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. **DATE** 8-24-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. 1) N_2, 2) rerun in N_2, 3) air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-19-H600
p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent, initial reflux

SIZE 10 mg.

X-AXIS

TEMP. SCALE 200 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

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

SUPPRESSION 0 mg.

RUN NO.

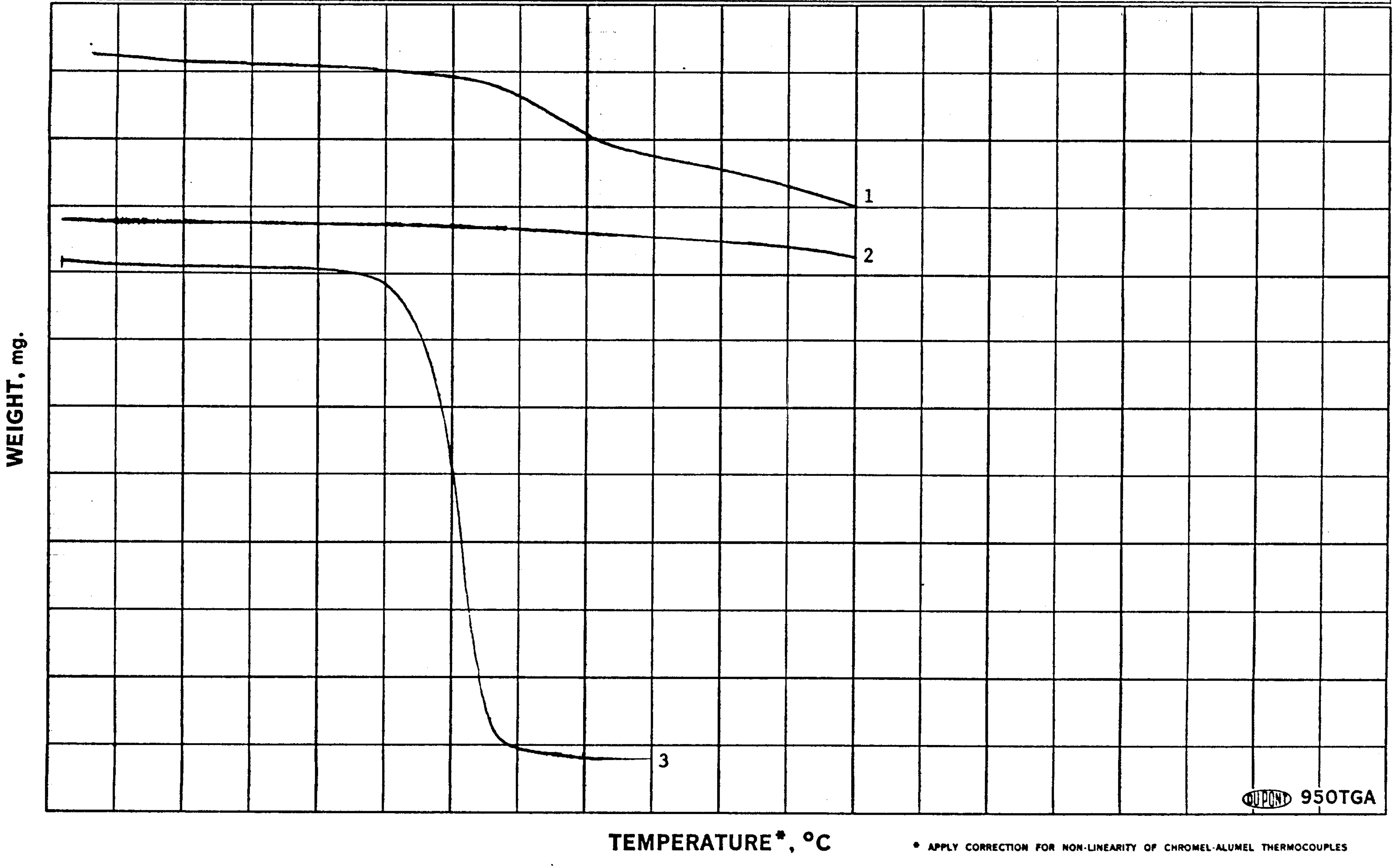
DATE 9-3-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. 1) N_2, 2) rerun in N_2, 3) air

TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 50

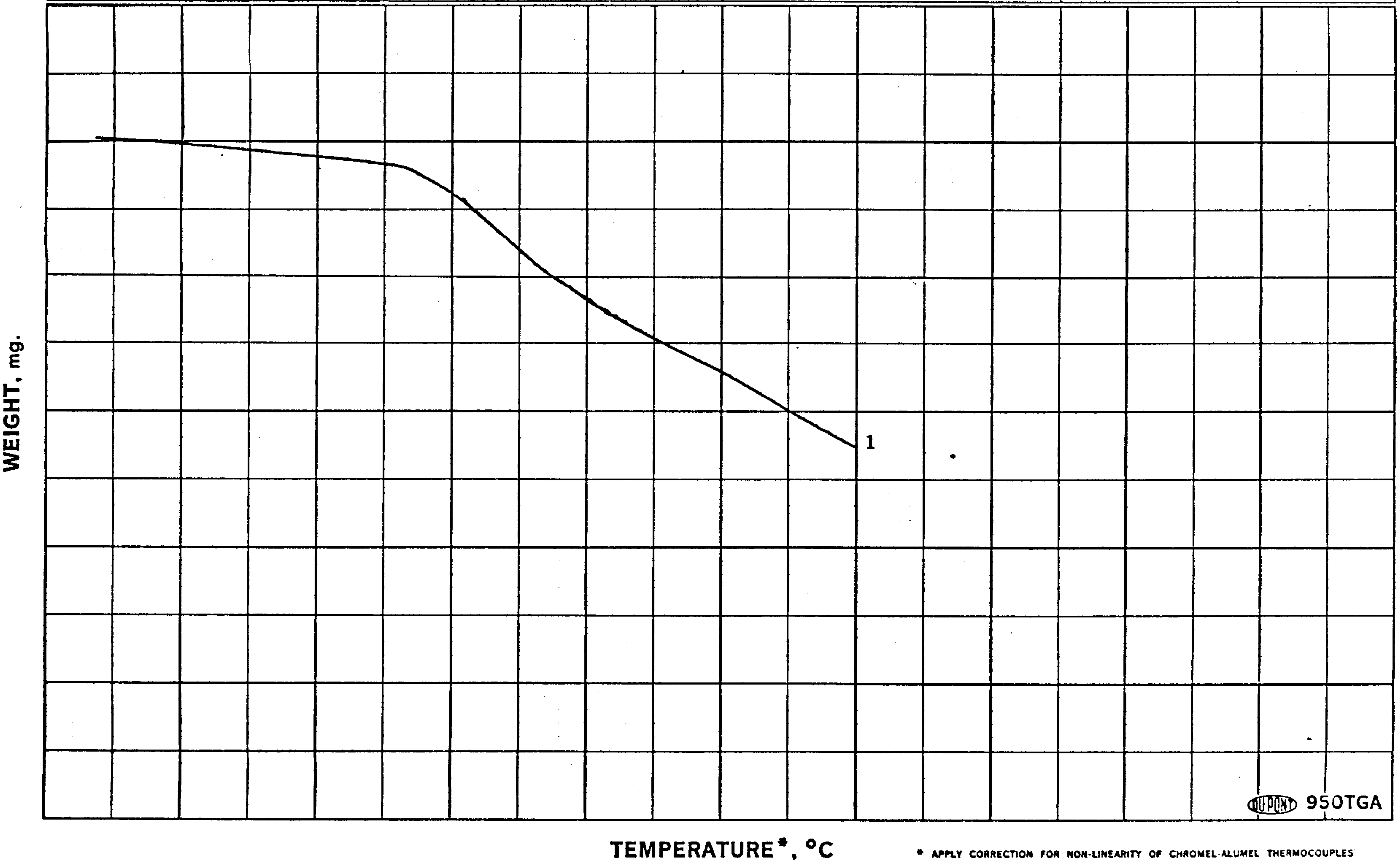
DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-37-20-H425
p-$(C_6H_5\text{-}CH{=}N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
$ZnCl_2$
no solvent (not recycled)
SIZE 10 mg.

X-AXIS
TEMP. SCALE 200 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. ______ DATE 8-26-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. nitrogen
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

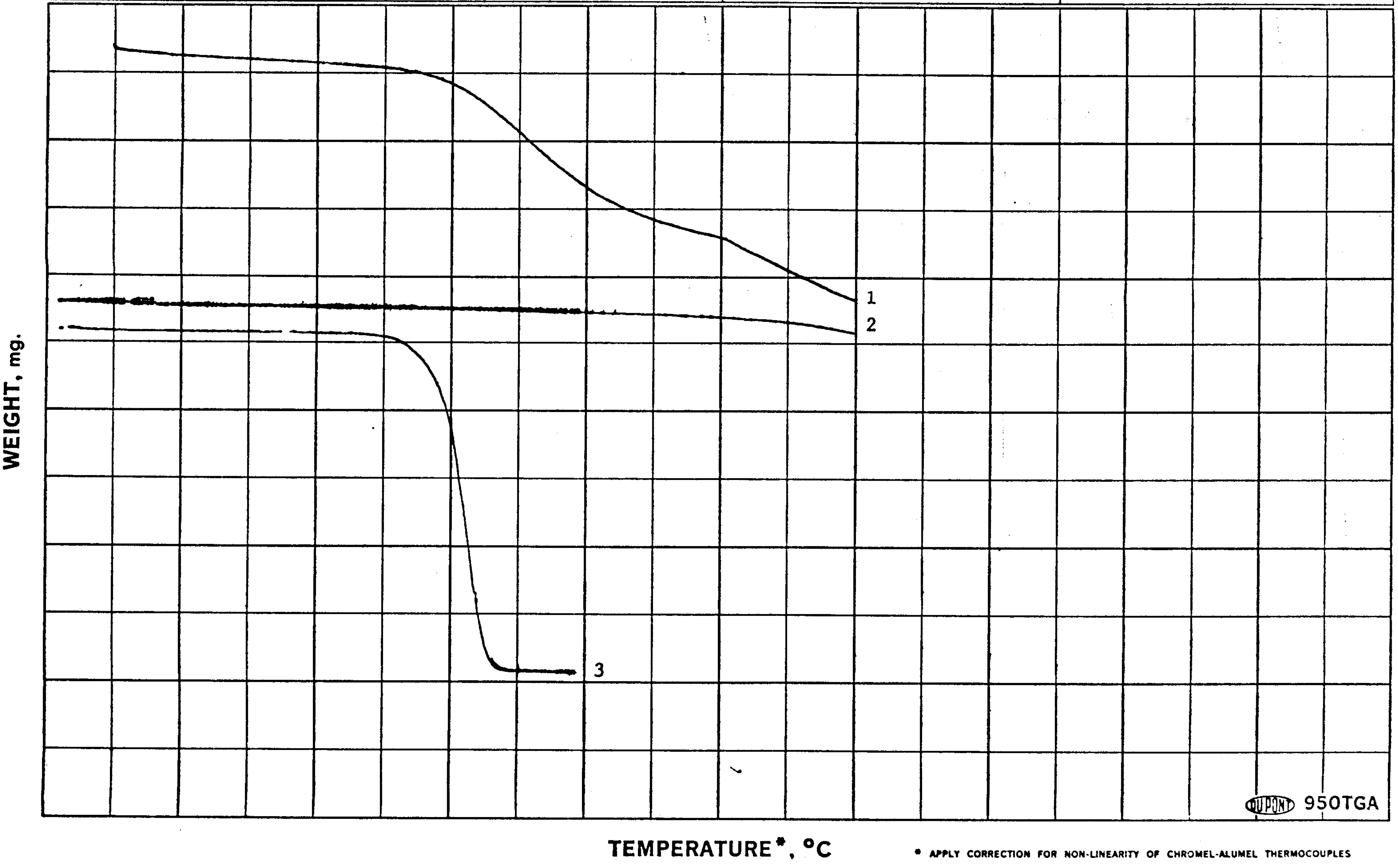
DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-37-21
p-$(C_6H_5$-CH=N$)_2C_6H_4$
p-[(n-BuO$)_2$CH$]_2C_6H_4$
C_6H_5N=CHC$_6H_5$
$ZnCl_2$
SIZE 10 mg.

X-AXIS
TEMP. SCALE 200 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. ______ DATE 8-26-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. 1) N_2, 2) rerun in N_2, 3) air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 52

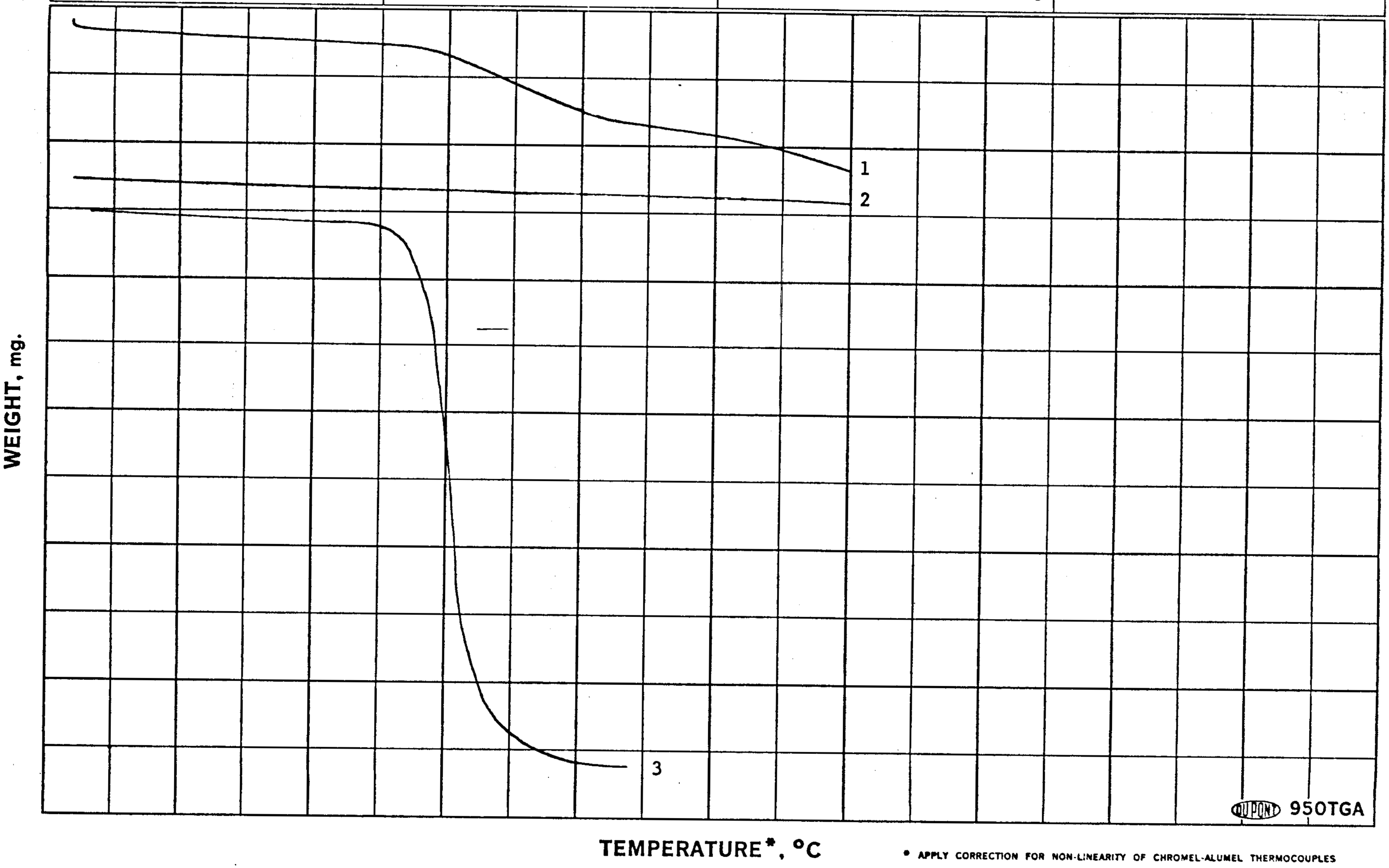
DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-37-22-H425
m-$(C_6H_5CH{=}N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
$ZnCl_2$
no solvent
SIZE 10 mg.

X-AXIS
TEMP. SCALE 200 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. **DATE** 8-12-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. 1) N_2, 2) rerun in N_2, 3) air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

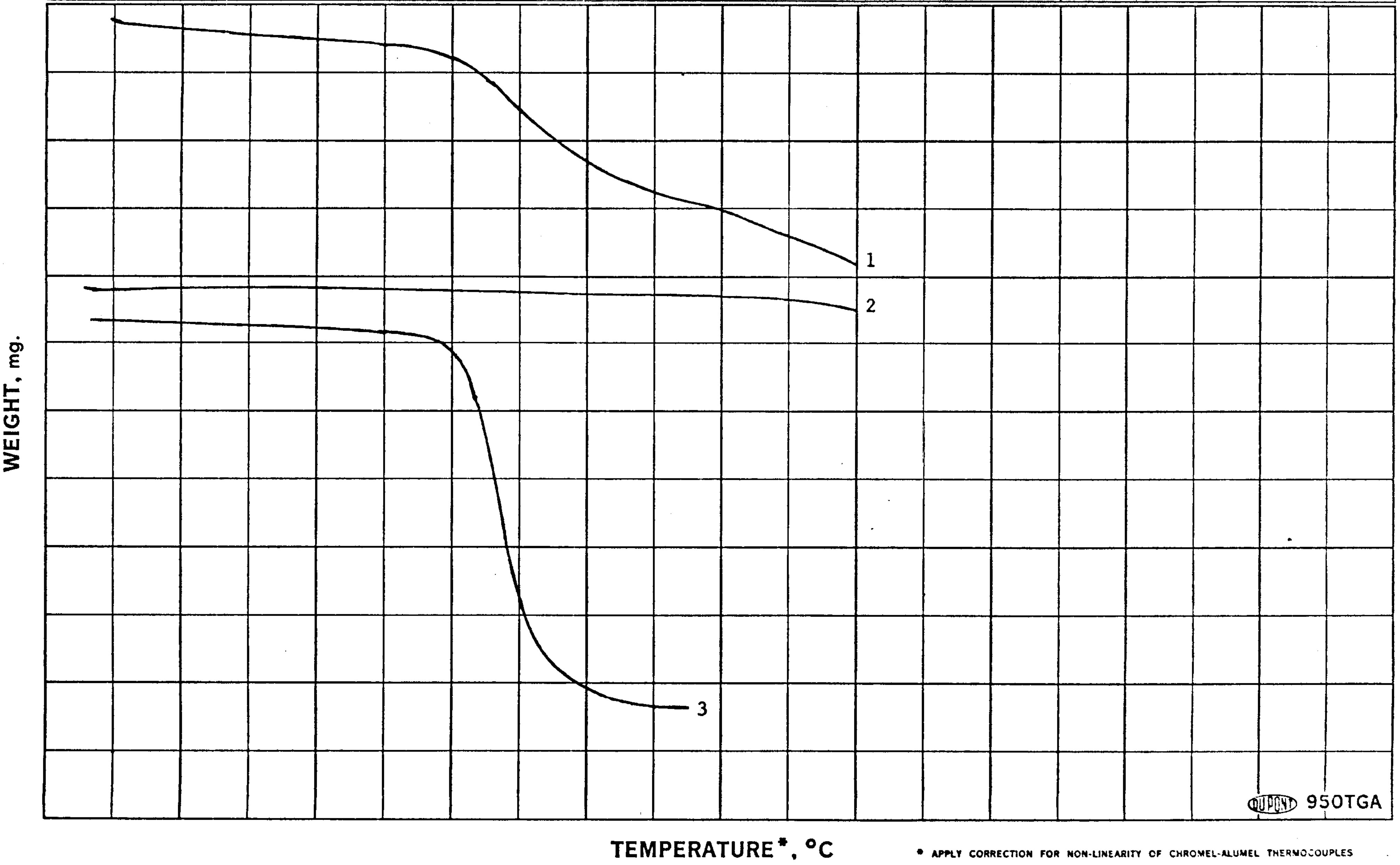
DUPONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-37-23-H425
m-$(C_6H_5\text{-}CH{=}N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
$C_6H_5N{=}CHC_6H_5$
$ZnCl_2$
SIZE 10 mg.

X-AXIS
TEMP. SCALE 200 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO.
DATE 8-12-65
OPERATOR TO
HEATING RATE 15 °C/min.
ATM. 1) N_2, 2) rerun in N_2, 3) air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-37-24
p-$(H_2N)_2C_6H_4$
p-$[(n\text{-}BuO)_2CH]_2C_6H_4$
no solvent
yellow polymer

SIZE 10 **mg.**

X-AXIS

TEMP. SCALE 200 **°C/inch**

SHIFT 0 **inch**

TIME SCALE (ALT.) 0

Y-AXIS

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

SUPPRESSION 0 **mg.**

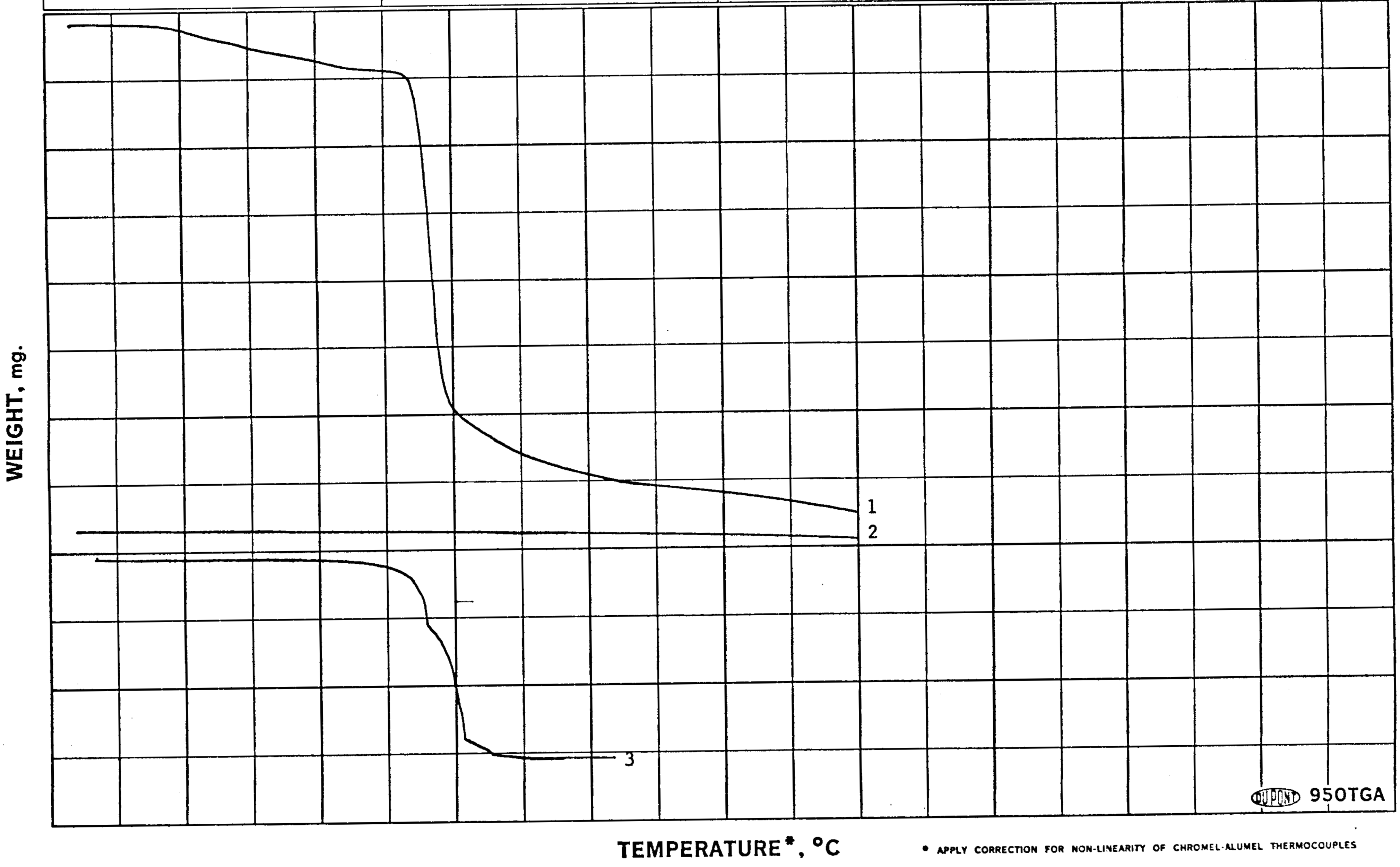
RUN NO. **DATE** 8-11-65

OPERATOR TO

HEATING RATE 15 **°C/min.**

ATM. 1) N_2, 2) rerun in N_2, 3) air

TIME CONSTANT 2 **sec.**



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 54