REPORT

ON

THE

FUNDAMENTAL STUDIES ON THE SYNTHESIS OF HEAT-RESISTANT POLYMERS

TO

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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PERFORMED

UNDER

NASA GRANT NsG339

SEPTEMBER, 1965

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA 46556

PROGRESS REPORT NUMBER 6

ON THE

FUNDAMENTAL STUDIES ON THE SYNTHESIS OF HEAT-RESISTANT POLYMERS

THE SYNTHESIS AND EVALUATION OF POLYMERIC SCHIFF BASES BY BIS-SCHIFF BASE EXCHANGE REACTIONS

PERFORMED

UNDER

NASA GRANT NsG339

BY

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PRINCIPAL INVESTIGATOR

DEPARTMENT OF CHEMISTRY

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NOTRE DAME, INDIANA 46556

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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.

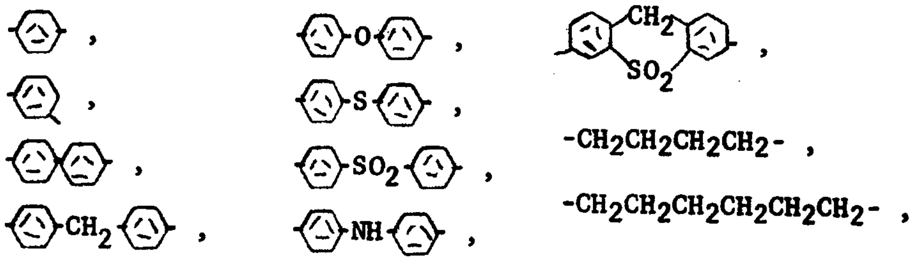
This report covers studies performed by G. F. D'Alelio and J. Crivello.

Date September 15, 1965

Signed G F D'Alelio
G.F. D'Alelio
Principal Investigator

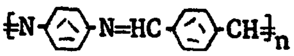
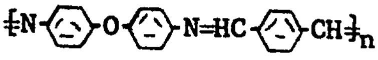
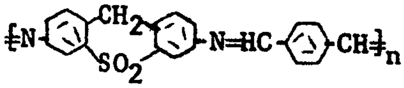
ABSTRACT

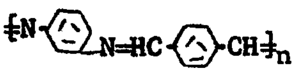
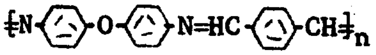
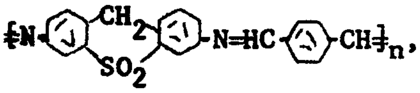
Three new bis-Schiff base monomers were synthesized, completing the series of eleven monomers required for the polymer syntheses. Eleven Schiff-base polymers of the general structure,  were synthesized by both the bis-Schiff base exchange melt and the solution methods. In these polymers, -Z- represents the following structures:

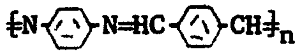
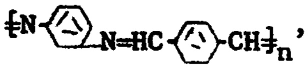


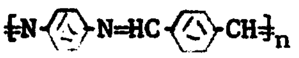
representing polymers which contained conjugated, pseudoconjugated or non-conjugated backbone structure.

The thermal resistances in nitrogen and in air of the non-conjugated aliphatic polymers are much lower than those of the conjugated and pseudoconjugated polymers. Also, the thermal resistance in air and in nitrogen of the conjugated and pseudoconjugated polymers prepared in solution is much lower than the same polymers prepared by melt bis-Schiff base exchange procedures.

Both the conjugated and pseudoconjugated polymers prepared by bis-exchange reactions have very good thermal stabilities in nitrogen and in air; the highest values, however, are found in the conjugated polymers. When these polymers are condensed to a temperature of 400°C (752°F), the best conjugated polymer,  shows a heat-resistance in nitrogen of 550°C (1022°F) compared to the two best pseudoconjugated polymers,  and  which have a resistance in nitrogen of 525°C (977°F); while in air, the best conjugated polymer,

 shows a heat-resistance of 500°C (932°F) compared to the best pseudoconjugated polymers,  and , both of which show a heat-resistance of 475°C (877°F) in air.

When the conjugated and pseudoconjugated polymers are condensed to higher temperature by postheating to 600°C, their thermal stabilities in nitrogen and in air are increased. The two conjugated polymers,  and , which have been condensed to 600°C, show heat-resistances in nitrogen of 630°C (1066°F) and 645°C (1103°F) respectively, compared to a value of 550°C (1022°F) for the pseudoconjugated polymer, .

When the conjugated and pseudoconjugated polymers are condensed to 1176°C by postheating, all the polymers so treated show a heat-resistance in nitrogen of about 1176°C (2026°F) with losses averaging about 3.0% of the polymers; with the conjugated polymer,  showing the highest thermal stability of 600°C (1112°F) in air.

Some secondary reaction appears to occur when the polymers are heated in nitrogen to temperatures above 600°C and the resulting polymers, even when heated to 1176°C, are not typical chars but retain their bright, shiny appearance.

The polymer prepared from dibenzylidene-m-phenylenediamine appears to have heat-resistance comparable to the p-phenylenediamine derivative, and because of lower cost of the meta compound, its future use is indicated.

Preliminary experiments indicate that the syntheses of the bis-Schiff bases can be circumvented by reacting all the reagents, namely, the aryldiamine, the terephthaldehyde, the aniline, and the benzaldehyde directly in a one-step melt process.

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I. Introduction.

Previous reports[1,2] on the syntheses of heat-resistant polymers describe the various reactions applicable to the syntheses of polymeric Schiff bases. Based on these investigations, three areas were selected for further studies.[2]

The first area, dealing with an exchange reaction between two difunctional Schiff bases which yield[1,2] black polymeric Schiff bases that pass through a fusible stage, is the subject of this report.

A second area, "The Synthesis and Evaluation of Polymeric Schiff Bases from Xylylidene Tetraalkyl Ethers", is the subject of a separate report.[3]

A third area of investigation, "Preliminary Studies on the Synthesis and Evaluation of Polymeric Azines", is also the subject of a separate report.[4]

This report concerns investigations on the synthesis of polymeric Schiff bases by bis-Schiff base exchange reactions and an evaluation of the heat-resistant properties of the polymers so synthesized.

When two bis-Schiff bases react, one containing an aromatic dialdehyde moiety and the other an aromatic diamino moiety, the resulting product is a stable, non-volatile poly-Schiff base. This polymerization reaction is described by the following equation:

$$n\ C_6H_5CH{=}NArN{=}CHC_6H_5 + n\ C_6H_5N{=}CHArCH{=}NC_6H_5 \longrightarrow$$
$$\left[NArN{=}CHArCH \right]_n + 2n\ C_6H_5N{=}C_6H_5 \qquad \text{(eq. 1)}$$

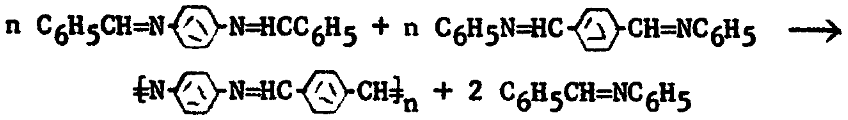
in which Ar represents a divalent aromatic moiety. Thus, the end groups of each of the two reacting monomeric bis-Schiff bases combine together to give rise to two equivalents of a more simple volatile Schiff base. The driving force of the reaction can be attributed to two factors; the formation of a very stable polymeric Schiff base and the removal of simple volatile Schiff base by distillation. A number of monomers, in which the terminal groups of the aromatic diamine Schiff base are $C_6H_5CH{=}$ groups, and of the aromatic dialdehyde are $C_6H_5N{=}$ groups, respectively, are discussed in previous reports.[1,2]

Most of the earlier work[1,2] on the synthesis of the poly-Schiff bases by the bis-exchange reaction used reagents in which the Ar moiety was phenylene, $-C_6H_5-$, thus

$$n\ C_6H_5CH{=}NC_6H_4N{=}HCC_6H_5 + C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5 \longrightarrow$$

$$\text{+}NC_6H_4N{=}HCC_6H_4CH\text{+}_n + 2n\ C_6H_5CH{=}NC_6H_5 \qquad \text{(eq. 2)}$$

Further, both reactants, the dibenzalphenylene diamine, , and the xylylidenedianil, , were para derivatives, to yield a para-para type polymer, thus:

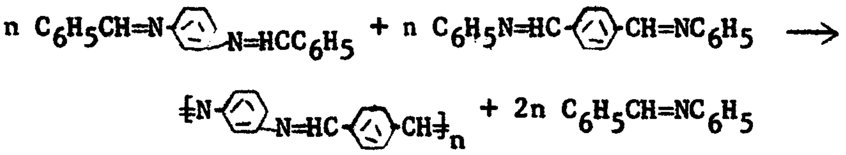


(eq. 3)

para-para polymer

The para derivatives were deliberately chosen on the expectation that the resulting polymer would possess the highest degree of linearity as a result of bond angles. It was expected that such a degree of linearity would contribute to maximum heat resistance.

It was indicated in a previous report[2] that, in the reaction with xylylidene tetramethyl ether, meta phenylenediamine and its dibenzylidene derivative appeared to be better reactants than their analogous para compounds because the meta compounds permitted a longer fusi ble stage during the polymer synthesis. As seen from the following equation, the conjugation in the resulting meta-para polymer would not be interrupted by the use of the meta diamine derivative:

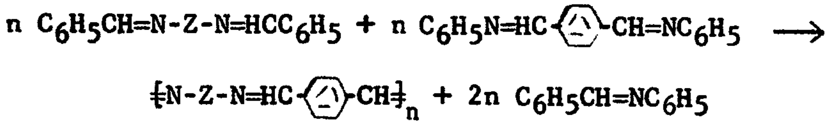


meta-para polymer (eq. 4)

Accordingly, it was one purpose of this study to compare the dibenzylidene derivatives of meta and para phenylenediamine in the polymerization reaction and to evaluate the differences, if any, in the thermal resistances of the resulting polymers. It will also be noted that present studies were limited to the para derivative for the dialdehyde moiety, namely, the p-xylylidenedianil aniline. This restriction exists for the present only, because the unavailability of the metaphthaldehyde. It is obvious that its use as a reagent with the meta and para diamines would produce meta-meta and para-meta type polymers respectively, which ultimately should be compared to the para-para and meta-para polymers. At the onset of the studies detailed in this report, it was not deemed advisable to dilute or divert the program to synthesize the meta-dialdehyde until evaluation of the meta-para type polymer have been completed. Then, if the meta-para type polymer were shown to have properties similar to the para-para polymers, future research would be devoted to the syntheses of meta-meta and para-meta Schiff base polymers.

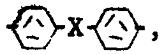
An examination of equations 3 and 4 will show that the conjugation in the polymer is uninterrupted, that is, either a carbon-to-carbon double bond, C=C, or a carbon-to-nitrogen double bond, C=N, alternate with a carbon-to-carbon, C-C, single bond, or with a carbon-to-nitrogen single bond, C-N. Since the heat resistance[1,2] as well as their semi-conductor properties,[2] have been attributed to this uninterrupted conjugation, it was considered important to determine how the heat resistance of these polymers would be influenced by decreasing or interrupting the conjugation by inserting appropriate groups or structures in the backbone of the polymer. For the study of this specific phase, it was decided to maintain the dialdehyde moiety, =HC-⌬-CH=, constant in the polymer structure and to introduce the changes in the conjugation in the diamine moeity, =N-Z-N=, to yield polymers of the general structure, {N-Z-N=HC-⌬-CH}$_n$, wherein Z would represent the structure in which the changes in conjugation would be introduced.

It was also a purpose of this study to evaluate the bis-exchange reaction in the syntheses of these polymers to determine the breadth of the applicability of the bis-Schiff base exchange polymerization reaction, thus

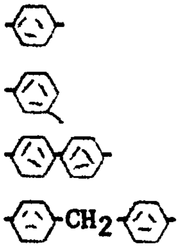


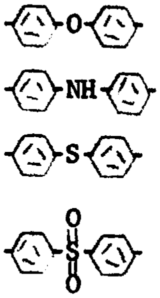
(eq. 5)

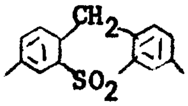
Polymers in which Z is the phenylene group, $-C_6H_4-$, as given in equations 3 and 4, would thus become the reference point for the studies on the effects due to changes in the nature or the extent of conjugation. The conjugation can be effectively interrupted, completely by eliminating the arylene group as the Z structure between the nitrogen atoms and substituting therefore, an alkylene group, $\left(CH_2 \right)_n$. Two such -Z- structures, $-(CH_2)_4-$ and $-(CH_2)_6-$ were selected for evaluation as representing non-conjugated polymers of the general structure .

A relatively simple method of changing the character and extent of conjugation in aromatic compounds is to introduce changes in diphenyl,  by insertion of other atoms or groups of atoms, such as -O-, -S-, $-SO_2-$, $-CH_2-$, -NH-, etc. between the benzene rings so that they are bonded to the benzene rings by single bonds only, thus, , to give polymers of the general structure, $\left[N-C_6H_4-X-C_6H_4-N{=}HC-C_6H_4-CH \right]_n$. Since a number of these X groups contain atoms with unshared pairs of electrons which can contribute to resonance structures, they cannot be considered as completely non-conjugated; rather, because of their character, they can be considered as "pseudoconjugated" and more closely related to  and to  rather than to the aliphatic $\left(CH_2 \right)_4$ and $\left(CH_2 \right)_6$ structures.

Accordingly, for this study dealing with conjugation, polymers were prepared which contained the following Z structures:







$-CH_2CH_2CH_2CH_2-$

$-CH_2CH_2CH_2CH_2CH_2CH_2-$

The syntheses of some of these polymers required the synthesis of some new polymers.

Another purpose of this research was to attempt to produce by the bis-Schiff base exchange reactions, black polymers which pass through a fusible stage, in those reactions which yield conjugated or pseudoconjugated structures and to compare their thermal properties with the corresponding polymers made directly from the dialdehyde and the diamine by solution polymerization. As shown in previous reports,[1,2] Schiff base polymers prepared by solution methods are of the infusible, insoluble, light colored, brick-dust type of lower molecular weight than the black polymers prepared by melt or exchange methods. In the specific case of $\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$, the solution polymer is of yellow color, whereas the polymer prepared by a bis exchange reaction passes progressively from a yellow to an orange to a brown to a black polymer as the polycondensation proceeds.

II. Synthesis of Monomers.

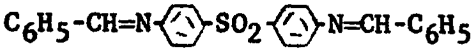
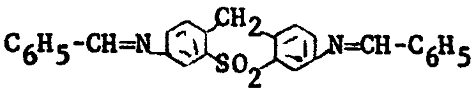
The synthesis of the following monomers used in this study was given in previous reports:[1,2]

Compound	Exper. No.	M.P. °C	Reference
$p\text{-}C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$	DA-24-42	78	1
$p\text{-}C_6H_5CH{=}NC_6H_4N{=}HCC_6H_5$	DA-24-43	140	1
$m\text{-}C_6H_5CH{=}NC_6H_4N{=}HCC_6H_5$	DA-24-44	104-106	1
$p\text{-}C_6H_5CH{=}NC_6H_4CH_2C_6H_4N{=}HCC_6H_5\text{-}p$	DA-29-176	130	2
$C_6H_5CH{=}N(CH_2)_4N{=}HCC_6H_5$	DA-29-178	26-27	2
$C_6H_5\text{-}CH{=}N(CH_2)_6N{=}HCC_6H_5$	DA-29-181	25	2
$p\text{-}C_6H_5CH{=}NC_6H_4OC_6H_4N{=}HCC_6H_5\text{-}p$	DA-29-184	182-183	2
$p\text{-}C_6H_5CH{=}NC_6H_4NHC_6H_4N{=}HCC_6H_5\text{-}p$	DA-29-188	183-186	2

Three new pseudoconjugated monomers for use in the current studies were also synthesized by the continuous azeotrope method used so successfully previously.[1] The diamine and benzaldehyde, in a molar ration of 1:2 respectively, were refluxed together in benzene in an apparatus to which was attached a Dean-Stark trap to collect the evolved water. When the theoretical amount of water had accumulated in the trap, the reaction mixture was allowed to cool, the product removed by filtration and recrystallized from benzene to a constant melting point. In all cases the yield of crude product was substantially theoretical. In some cases, difficulties encountered in recrystallization resulted in a low yield of recrystallized product. The data is summarized in Table 1.

Table 1

Data on Some New Bis-Schiff Base Monomers

Monomer	Exper. No.	% Yield Product		Melting Point, °C		Ref. no.
		Crude	Recrys.	Found	Ref.	
	DA-42-12	100	41.8	180	178	5
	DA-29-272	100	42.4	236	232	6
	DA-42-7	100	93.4	208	--*	-

* Analysis: Theory: C, 74.50; H, 4.58; N, 6.44; S, 7.35.
Found: C, 74.47; H, 4.65; N, 6.48; S, 7.44.

III. Polymerization Reactions.

A. Melt Polymerizations.

Three separate routes for the synthesis of Schiff base polymers by exchange reactions, namely, the amine exchange, the carbonyl exchange, and the bis-Schiff base exchange reactions were described in previous reports.[1,2] On the basis of these studies, the bis-Schiff base exchange reaction was selected as the most advantageous method for the preparation of the polymers. Though the amine exchange and the carbonyl exchange reactions proceed much more rapidly than the bis-exchange reaction, they are more difficult to control and in most cases produce a heterogeneous intermediate condensation product unless the reaction is performed in the presence of an active solvent such as benzalaniline. On the other hand, the bis-Schiff base exchange reaction proceeds very smoothly in the absence of benzalaniline, yielding homogeneous intermediate condensation products telomerized by the benzal and anilido moieties in a medium of by-product benzalaniline generated by the reaction. The bis-Schiff base exchange reaction is much slower than either the amine or the aldehyde exchange, but it can be accelerated by Lewis acids such as zinc chloride and toluene sulfonic acid. Since the purpose of this study was to compare the properties of a number of polymeric Schiff bases having substantially different backbone structures, it was considered necessary to select arbitrarily some of the reaction conditions for the polymerization which tend to equalize the diverse nature of the various dibenzylidene monomers. Because of the diverse natures of the dibenzylidenediamine monomers and the lack of knowledge of the interaction of such an active solvent as benzalaniline with these monomers, it was decided to perform the polymerization in the absence of benzalaniline. Also, it was considered that the uncatalyzed polymerizations would introduce less complications. Accordingly, it was decided to perform uncatalyzed, unsolvated polymerizations. With this decision it became necessary to select time-temperature conditions under which all or most of the desired polymers would be synthesized.

Previous studies have shown[1,2] that polycondensation reaction involving exchange reactions is not completed at 325°C and the black polymers can undergo postcondensations in the solid state to tough polymers. Accordingly, a number of preliminary experiments in these studies showed, on the basis of preliminary thermogravimetric analyses, that the condensation is far from complete unless the temperature of condensation exceeds 400°C; in fact, it is not truly completed until the temperature of condensation approaches the 600°C region. This was evidenced by the continued elimination of benzalaniline when the polymeric Schiff bases synthesized by the bis-Schiff base exchange reactions, were heated to 1200°C in nitrogen in the thermogravimetric apparatus; these same preheated polymers, when reheated to 1200°C, showed minor heat losses.

On this basis, it was decided to prepare all the polymers under the identical temperature conditions of condensation up to 400°C under a standardized time and pressure schedule which would be maintained uniformly for all the polymerizations, whenever feasible. The polymers prepared up to a condensation temperature of 400°C would then be isolated and a portion would be postheated to 600°C. A temperature of 650-700°C would have been preferable to 600°C as the selected second higher 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 electric heating mantle surrounding the aluminum block.

It was considered advisable also to complete the condensation further at some temperature in excess of 600°C and preferably to the region of 1000°C or higher. This required the development of a special procedure and it was accomplished by heating small samples of the order of 10 mg. of the polymer directly in a thermogravimetric apparatus.

It was realized that in utilizing a standardized 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 by distillation or sublimation, 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, if condensation reaction is continued far enough, for evaluation of thermal properties.

1. Standardization of Polymerization Procedure.

a. Experimental.

The reagents were placed in a reaction 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 reaction tube, and a probe hole was located within one-half inch of the inserted reaction tube. The metal cube was heated by a special Glas-Col square mantle, custom-made for the cube.

Temperatures up to 400°C were maintained and controlled by a Model 1422-071 Temperature Controller from Cole-Parmer Instrument and Equipment Company. For heating above 400°C, the temperature was controlled by a Variac and the temperature determined by a thermocouple. The maximum range of the apparatus equipped with quartz reaction tubes is 600°C.

The reaction tube was 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 dioxane-acetone trap. All joints were ground glass and standard taper.

A number of polymerizations, DA-29-244, DA-29-247, DA-29-262, DA-29-264 and DA-29-265 were performed in this apparatus in which the time, temperature and pressure cycles were varied over a wide range.

An evaluation of these polymerizations with respect to overall behavior such as ease of control, yield, etc., led to the selection of the standard conditions for all subsequent melt polymerization except those involving the aliphatic amine derivatives. The standardized conditions are shown in Table 2.

Table 2

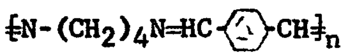
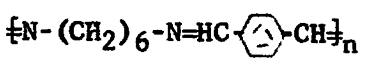
Standardized Melt Polymerization Conditions Using
Bis-Schiff Base Exchange Reactions

Time (hours)	Temperature (°C)	Pressure
2	200	atmospheric
2	260	atmospheric
10	320	atmospheric
20	380	1 mm
20	400	1 mm

Under these standardized conditions, the polymerizations were found to proceed smoothly through the successive color changes from yellow to red to brown to black with the continuous evolution of benzalaniline. It is necessary to exercise care during the fourth stage of the polymerization when the pressure is reduced to avoid loss of reactants due to bumping of benzalaniline. It was found advisable to reduce the pressure slowly in successive stages over the course of about one-half an hour.

2. Standardized Polymerizations.

The polymers were prepared by the bis-Schiff base exchange reaction under melt conditions according to equation 5. The standardized condition was used in all cases except in the cases of the two polymers which contained aliphatic moieties in their backbone, namely:

 and 

in which case decomposition was found to occur under these conditions.

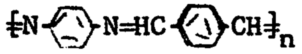
However, it was found possible to synthesize these "aliphatic" Schiff bases under modified conditions which consisted primarily in lowering the temperature and decreasing the time of reaction. The modified conditions are shown in Table 3.

Table 3

Conditions for Preparing "Aliphatic" Schiff Base Polymers

Time (hours)	Temperature (°C)	Pressure
2	150	atmospheric
10	200	atmospheric
10	250	1 mm

The polymers prepared by the bis-Schiff base exchange reactions under melt conditions using standardized and modified standardized conditions, together with other pertinent information, is shown in Table 4. The general procedure consisted in mixing the reagents in the reaction vessel, evacuating the system, sweeping out the system with nitrogen and performing the polymerization under a nitrogen atmosphere under the selected conditions of temperature, pressure, and time. The polymerizations were carried out on a relatively small scale of 0.005 mole with respect to the monomers.

To determine whether or not changes in the standardized polymerization conditions would introduce changes in the heat resistance properties of the aromatic-type black, Schiff base polymers, Experiment DA-29-154 was performed to synthesize  under non-standard, that is, modified conditions.

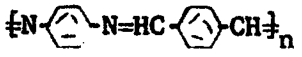
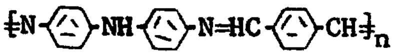
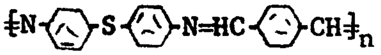
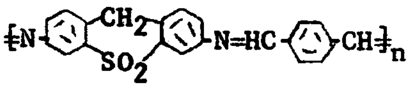
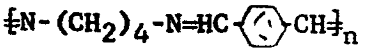
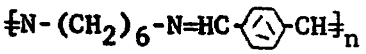
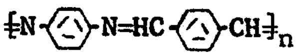
Experiment DA-29-154 corresponds to DA-43-13 in the reagents used but differs in the history of its polymerization conditions which are as follows:

Time (hours)	Temperature (°C)	Pressure
4	200	atmospheric
8	280	atmospheric
10	320	atmospheric
5	400	atmospheric
19	450	1.5 mm

The yield of black, shiny polymer was 127.7% of theory.

Table 4

Polymers Prepared by Bis-Schiff Base Exchange Reactions

Polymer	Exper. No.	% Yield	Color	Polymerization Conditions
	DA-42-13	109.7	black	standardized
	DA-42-14	105.0	black	standardized
	DA-29-284	106.4	black	standardized
	DA-29-265	105.4	black	standardized
	DA-29-275	110.0	black	standardized
	DA-29-282	98.3	black	standardized
	DA-42-16	100.0	black	standardized
	DA-29-285	89.6	black	standardized
	DA-42-11	105.0	black	standardized
	DA-29-286	79.8	orange	modified standardized
	DA-42-10	102.0	orange	modified standardized
	DA-29-154	127.7	black	modified standardized

The bis-Schiff base exchange reaction was found to go well for all the monomers tried. For the conjugated and pseudoconjugated monomers, the polymerization was found generally to proceed through five stages:

1) the formation of a yellow melt;
2) changing to an orange melt;
3) the formation of a red-brown melt;
4) becoming dark brown; and
5) finally becoming a black, shiny, porous solid.

In contrast, the aliphatic, non-conjugated polymers were orange in color when the polymerizations were terminated.

In agreement with previous results,[1,2] the yields of polymer were found generally to be in excess of 100% of the theoretically calculated value for a DP of ∞ due to the difficulty of removing the by-product, benzananiline, from the polymer mass and to the incompleteness of the condensation at these temperatures.

Yields lower than 100% of theory can be attributed to loss of uncondensed reagents during the distillation stage under reduced pressure in the polymerization procedure. Later studies show that grinding these polymers and subjecting them to higher temperatures and lower pressures, the condensation reaction can be continued and more benzalaniline by-product obtained.

3. Miscellaneous Polymerizations.

A number of other polymerizations were performed to explore and extend the scope of the bis-exchange polymerization. Since the Schiff base exchange reactions were shown to be very facile reactions, it was believed that it would be unnecessary to prepare each of the monomers, p-xylylidenedianil and dibenzylidene-p-phenylenediamine separately for polymerization. It might be possible that these monomers could be prepared in situ from the constituent p-phenylenediamine, terephthaldehyde, benzaldehyde and aniline. Exchange would then take place between the various Schiff bases formed in the reaction mixture giving rise to the most stable end-product, the polymer.

To evaluate this concept, three polymerization reactions were performed.

a. Experimental.

i. (DA-29-252) Melt Polymerization of p-Phenylenediamine, Terephthaldehyde, Aniline, and Benzaldehyde.

Equimolar quantities (0.004 M) of each of the following compounds were weighed out and placed into the reaction tube in the following order: benzaldehyde, aniline, p-phenylenediamine, and terephthaldehyde. A yellow color immediately was formed and the reaction mixture solidified. The reaction tube was fitted with a condenser, a receiver and a nitrogen inlet and the reaction mixture subjected to a melt polymerization under the following conditions:

Time (hours)	Temperature (°C)	Pressure
2	220	atmospheric
8	320	atmospheric

During the eight-hour heating period, the polymer melt was observed to undergo a change in color from yellow to brown-black. When the reaction was discontinued, benzalaniline and water were found in the receiver and 0.824 g. (102% yield) of amorphous polymer was obtained.

ii. (DA-29-256) Repeat of DA-29-252 Using a Different Procedure.

The same quantities of reagents were used in this polymerization as in DA-29-252. The method of the addition of reagents, however, is different. The two amines, p-phenylenediamine and aniline were placed in a small mortar, then the mixture of benzaldehyde and terephthaldehyde was added with rapid stirring by means of a pestle. The mixing was accompanied by immediate formation of a yellow color in the pasty mass. After about five seconds the mixture solidified, was removed from the mortar, placed in a reaction tube and melt polymerized under the following conditions:

Time (hours)	Temperature (°C)	Pressure
2	220	atmospheric
2	220-400	atmospheric
9	400	atmospheric
10	400	atmospheric
4	400	1.5 mm

After the completion of the reaction benzalaniline was found in the receiver and aniline and water in the dry ice-acetone trap. A black, dull, amorphous-appearing polymer was obtained in a 100% yield.

iii. (DA-29-260) Melt Polymerization Using m-Phenylenediamine, Aniline, Benzaldehyde, and Terephthaldehyde.

Four-thousandths of a mole of each of the amines, m-phenylenediamine and aniline, were placed in a mortar and then a mixture of 0.004 mole of each of the aldehydes, benzaldehyde and terephthaldehyde, were added. Mixing by means of a pestle produced a yellow, very viscous, sticky oil which would not solidify at room temperature on standing. The reaction mixture was removed from the mortar as glassy chips by cooling the mortar in dry ice. The cold, glassy oligomer was transferred to a reaction tube and polymerized under the following conditions to yield a black, shiny polymer:

Time (hours)	Temperature (°C)	Pressure
12.5	260	atmospheric
1.0	370-390	atmospheric
7.0	414	atmospheric
9.0	360	1.5 mm

b. Discussion.

The three experiments described above show that it is possible to obtain Schiff base polymers by a route which by-passes the initial synthesis of Schiff base monomers. The reactions involved in this synthesis are a mixture of three Schiff base exchange reactions as well as the simple condensation of an aldehyde and an amine.

Of the three experiments performed above, the polymerization involving m-phenylenediamine (DA-29-260) is the best. This result probably arises from the maintenance of homogeneity throughout the polymerization due to the nature of the geometry of a polymer with m-phenylene units. This synthesis is deserving of future studies.

B. Solution Polymerization.

For purposes of this study, it was desired to compare the black Schiff base polymers prepared by the melt bis-Schiff base exchange reaction with the "yellow" infusible, brick-dust polymers prepared by another method. Since solution polymerization methods were shown[1,2] in the case of terephthaldehyde and phenylenediamine to yield such yellow polymers, the solution method was used to prepare these polymers. The solution method of Davidov and his coworkers[7] was modified to the continuous azeotropic method previously reported.[1,2] The amines used in these syntheses were purified before use either by crystallization or by distillation. The terephthaldehyde was recrystallized from water before use.

1. Experimental.

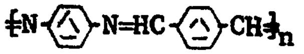
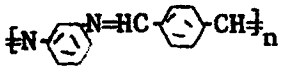
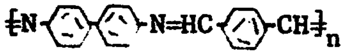
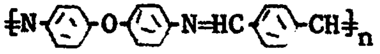
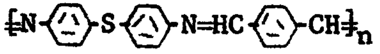
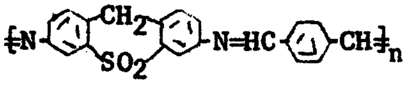
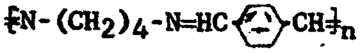
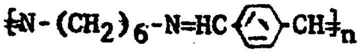
To a three-necked round-bottomed flask equipped with a condenser and a Dean-Stark trap is added 150 ml. of benzene and 0.005 mole of the appropriate diamine and the mixture heated to reflux temperature. Then terephthaldehyde (0.005 M) in 150 ml. of benzene was added to the amine solution by means of a dropping funnel while the mixture was vigorously stirred. The mixture was then refluxed for twenty hours; the azeotroped water collected in the Dean-Stark trap. The polymer appeared as a precipitate and at the end of the reaction it was removed by filtration, washed with benzene, and dried in a vacuum oven.

A modification of this procedure was used in the preparation of the solution polymer from 4,4'-diaminodiphenylamine since this monomer was obtained in the form of its sulfate salt. There was first dissolved in 250 ml. of water 0.02 mole of 4,4'-diaminodiphenylamine sulfate, which then was neutralized with an equivalent amount of sodium carbonate. Next, 0.02 mole of recrystallized terephthaldehyde was added and the entire mixture was refluxed for twenty hours. The orange polymer which precipitated during the reaction was recovered by filtration and washed with water. After drying 3.49 g. of polymer were obtained, representing a 58.7% yield.

Table 5 lists the polymers prepared by the solution method and gives yields and the color of the polymer.

Table 5

Polymers Prepared by Solution Method

Polymer	Exper. No.	% Yield	Color
	DA-29-94	98.4	yellow
	DA-29-276	82.6	yellow
	DA-29-277	55.2	yellow
	DA-29-266	92.3	yellow
	DA-29-278	32.6	yellow
	DA-29-281	58.7	orange
	DA-42-15	91.4	yellow
	DA-29-270	95.9	yellow
	DA-42-6	95.8	light green
	DA-29-269	86.8	white
	DA-29-268	81.0	white

2. Discussion.

Solution polymerization yielded a number of polymers with varying backbone structures. The color varies in these polymers depending on the amount of conjugation and upon the degree of polymerization. None of the solution polymers is black, indicating their low molecular weight and oligomeric character Most of the conjugated and pseudoconjugated oligomers are yellow, or near yellow such as orange or light green, while the oligomers containing aliphatic moieties in their backbones are white.

IV. Postheating of Polymers.

The polymers prepared under standardized polymerization conditions were condensed to a maximum temperature of 400°C. The black polymer, , DA-42-13 is one of these typical polymers. Preliminary thermogravimetric analyses in nitrogen of polymer DA-42-13 indicated that the polycondensation is not complete at this temperature and that a weight loss begins at about 600°C and levels off at about 800°C. When the same polymer, , DA-29-154 was prepared under modified conditions and condensed to a temperature of 450°C, the thermogravimetric analysis in nitrogen also showed that a weight loss began at about 600°C and levelled off at about 800°C, but that the weight loss was much less than the polymer condensed to 400°C. It was also observed that there was no substantial difference in the infrared spectra of the polymers condensed to temperatures of 400°C and 600°C.

These observations suggested that an evaluation should be made of polymers condensed to a temperature in the region of 600°C as well as to some temperature in the region of 1000°C or higher.

It would have been more desirable to have reacted the original reagents in a melt and condensed them directly to a temperature of 600°C or higher. The available polymerization apparatus permitted a maximum temperature of about

600°C. For heating to temperatures in excess of 600°C other means would have to be devised.

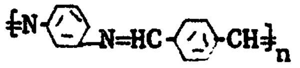
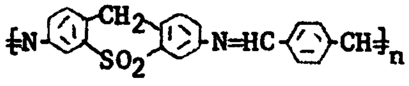
Since polymers which had been condensed to a temperature of 400°C were on hand, it was believed that the objectives of the study would be met in good measure by postheating the available 400°C polymers to 600°C and to some higher temperatures.

A. Postheating to 600°C.

The procedure for postheating the polymers prepared at 400°C consisted in grinding the polymers to a fine powder with a mortar and pestle, then placing in a quartz reaction tube similar in design and dimensions to the reaction tube used in the melt polymerization apparatus. This quartz reaction tube was equipped with the same accessories used for the melt polymerizations. After the samples were weighed into the quartz tubes, the nitrogen bleeder supported by a Teflon adapter and the other glassware was attached, then nitrogen was introduced into the system and the reaction tube inserted into the aluminum block which had already reached the desired temperature. The system was then placed under reduced pressure, and the polymers postheated at 600°C for twenty minutes at 1 mm Hg. Table 6 lists the polymers which were postheated to 600°C. The designation H600 is placed at the end of the number of the polymer to indicate that it has been postheated to 600°C.

Table 6

Polymers Postheated to 600°C at 1.0 mm Hg for Twenty Minutes

Exper. No.	Polymer
DA-42-13-H600	
DA-42-14-H600	
DA-42-42-H600	

B. Postheating to 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 400°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 adapted 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, after heating to 1176°C, are designated by the addition of R to the polymer number and are designated as recycles. Table 7 lists the specific polymers which were postheated to 1176°C.

V. Thermogravimetric Analyses.

It was predicted[1] at the beginning of this research that conjugated Schiff base polymers should show a high degree of thermal stability. This assumption was based both on theoretical considerations and upon the actual thermal stabilities of some conjugated polymers.[1]

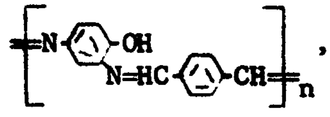
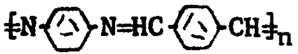
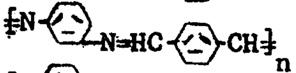
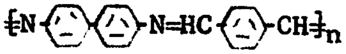
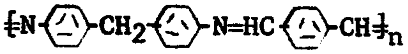
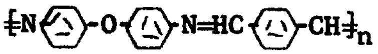
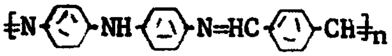
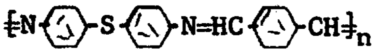
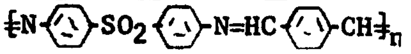
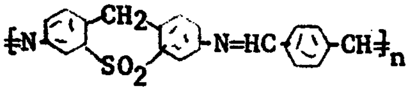
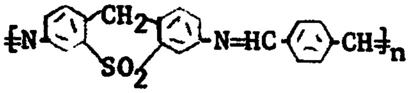
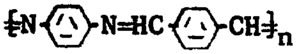
Since the start of this research some data has appeared in this area in the literature. This data, however, is limited to the infusible, insoluble brick-dust polymers of low molecular weight, and to independent methods of determining the thermal stability. Nonetheless, the data indicates that even low molecular weight Schiff base polymers possess significant thermal stability. Akitt and his coworkers indicate[8] that the polymer,  , has a thermal stability of the order of 300°C.

Table 7

Polymers Postheated to 1176°C in Nitrogen

Polymer Used	Exper. No.	Designation After Heating
	DA-42-13	DA-42-13-R
	DA-42-13-H600	DA-42-13-H600-R
	DA-42-14	DA-42-14-R
	DA-42-14-H600	DA-42-14-H600-R
	DA-29-284	DA-29-284-R
	DA-29-265	DA-29-265-R
	DA-29-275	DA-29-275-R
	DA-29-282	DA-29-282-R
	DA-42-16	DA-42-16-R
	DA-29-285	DA-29-285-R
	DA-42-11	DA-42-11-R
	DA-42-11-H600	DA-42-11-H600-R
	DA-42-154	DA-42-154-R

Topchiev and his coworkers report[9] a decomposition temperature for the low molecular weight yellow polymer obtained from the solution polymerization of terephthaldehyde and p-phenylenediamine to have a decomposition temperature of 350°C. Stivala, Sacco and Reich report[10] that the yellow polymer obtained from solution polymerization of m-phenylenediamine and terephthaldehyde in dimethylformamide and subsequently heated to 250°C in nitrogen is stable up to about 400°C.

In our studies, the thermal stability of the polymers was evaluated by thermogravimetric techniques. The du Pont 950 Thermogravimetric Analyzer in conjunction with a 900 Differential Thermal Analyzer was used to determine the thermal properties of the polymers at a heating rate of 15°C per minute. A number of thermogravimetric measurements were made in nitrogen and in air at gas flow rates of one (1) standard liter per minute. A sample weight of 10 mg was used in most determinations. A temperature correction has been made in the measurements for the non-linearity of the chromel-alumel thermocouples.

These studies consisted in performing thermoanalyses in a sufficient number of polymers to be able to correlate their thermal stabilities in nitrogen and in air to various experimental parameters such as

1) the degree of polymerization as reflected in color of the black polymers in contrast to the "yellow" or light-colored polymer,
2) the nature and extent of conjugation,
3) the final temperature of condensation used in the polymerization.

Accordingly, the studies were divided into the classification: a) melt and solution polymers; b) 600°C postheated polymers; c) 1176°C postheated polymers.

A. Melt and Solution Polymers.

The polymer prepared under melt polymerization conditions, namely, the black conjugated-type polymers condensed to 400°C and the aliphatic, non-conjugated polymers condensed to 250°C were thermoanalysed in nitrogen and in air and compared to their corresponding lighter-colored polymers prepared in solution. Table 8 summarizes and contrasts the thermal behavior of the melt (400°C) and solution polymers which were thermoanalyzed in nitrogen. The thermograms obtained for the respective polymers are given under the appendix number. Table 8 also gives the percentage of weight loss beginning at 200°C in increments of 100°C to the recorded limit of the apparatus of 1200°C, which has been corrected to 1176°C for the non-linearity of the chromel-alumel thermocouple. Table 9 summarizes and contrasts the thermal behavior of the melt (400°C) and solution polymers which were thermoanalyzed in air; the thermograms of the polymers thermoanalyzed in air are given under the appendix number .

Table 8

Per Cent Weight Loss of Melt and Solution Polymers at Various Temperatures While Being Heated in Nitrogen

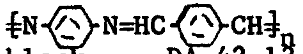
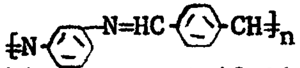
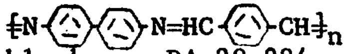
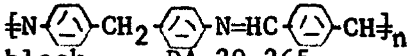
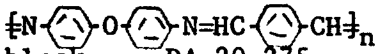
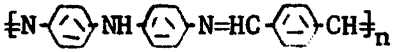
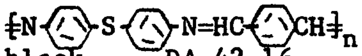
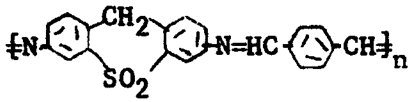
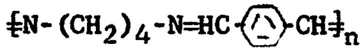
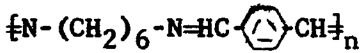
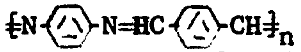
Polymer and Experiment No.		Weight Loss at °C											Appen. No.	Curve No.
		200	300	400	500	600	700	800	900	1000	1100	1176		
														
black	DA-42-13	---	0.0	1.2	2.4	10.0	18.4	22.0	23.4	24.4	26.6	29.4	1	1
yellow	DA-29-94	2.4	5.4	7.4	24.4	61.4	66.8	66.8	70.6	72.0*	----	----	5	
														
black	DA-42-14	---	0.0	0.6	0.6	9.2	14.8	18.6	20.4	21.6	25.6	28.6	7	
yellow	DA-29-276	0.6	3.0	4.4	33.6	42.6	47.6	49.4	50.6	51.6*	----	----	11	
														
black	DA-29-284	---	0.0	0.4	2.4	44.8	50.6	53.0	54.4	55.0	----	----	13	
yellow	DA-29-277	0.0	54.0	68.0	69.9	88.0	89.2	90.0	----	----	----	----	16	
														
black	DA-29-265	0.0	0.4	4.2	7.0	24.6	32.0	35.2	36.6	37.6*	----	----	18	
yellow	DA-29-266	0.0	0.0	0.4	41.0	64.6	67.6	68.4	70.6	71.6*	----	----	21	
														
black	DA-29-275	0.0	0.2	0.5	2.0	15.4	24.0	25.4	27.4	28.6	31.6	34.4	23	
yellow	DA-29-271	0.0	4.6	39.0	65.0	73.0	----	----	----	----	----	----	26	
														
black	DA-29-282	0.0	0.8	1.2	3.2	16.4	23.0	25.6	27.0	28.8	32.0	35.4	28	1
yellow	DA-29-281	2.0	6.4	8.0	45.8	63.0	69.4	----	----	----	----	----	30	
														
black	DA-42-16	0.0	0.0	0.6	2.4	12.6	22.2	26.4	28.4	30.0	32.4	35.0	32	1
yellow	DA-42-15	0.0	0.6	1.4	9.0	48.0	54.8	58.0	59.6	61.0*	----	----	34	1

Table 8

Per Cent Weight Loss of Melt and Solution Polymers at Various Temperatures While Being Heated in Nitrogen

Polymer and Experiment No.	Weight Loss at °C											Appen. No.	Curve No.
	200	300	400	500	600	700	800	900	1000	1100	1176		
													
black DA-29-285	0.0	0.0	0.2	2.2	11.6	17.6	21.2	22.6	24.6*	----	----	36	
yellow DA-29-270	0.6	2.6	9.0	25.0	61.0	65.0	66.4	67.2	69.6*	----	----	39	
													
black DA-42-11	0.0	0.6	0.8	1.4	13.5	15.0	19.2	22.4	28.6*	----	----	41	1
yellow DA-42-6	0.8	2.0	6.0	17.2	37.0	44.4	50.0	52.0	52.4*	----	----	45	
													
orange DA-29-286	0.6	2.0	18.0	60.0	71.0	84.0	85.4	----	----	----	----	47	
white DA-29-269	0.8	19.0	31.0	49.0	56.6	59.6	61.2	----	----	----	----	49	
													
orange DA-42-10	0.6	2.4	16.0	51.6	68.4	71.0	72.6	73.0	----	----	----	51	
white DA-29-268	0.8	8.0	20.4	62.0	72.8	74.2	74.8	----	----	----	----	53	
													
black DA-29-154	0.0	0.0	0.2	0.8	3.6	8.0	12.0	13.6	14.4	16.4	20.4	55	

* When the measurement was made on a scale of 100°C per inch, the maximum temperature recorded was 1000°C.

Table 9

Per Cent Weight Loss of Melt and Solution Polymers at Various Temperatures while Being Heated in Air

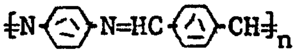
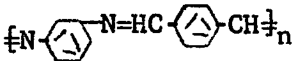
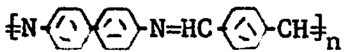
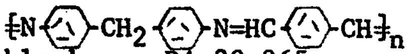
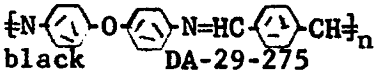
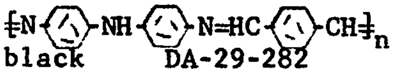
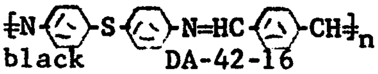
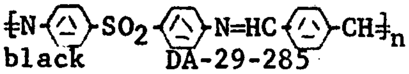
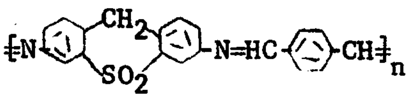
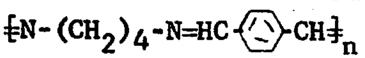
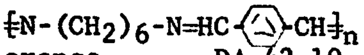
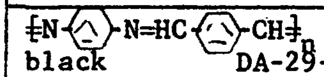
Polymer and Experiment Number	Per Cent Weight Loss at °C						Appendix Number
	200	300	400	500	600	700	
							
black DA-42-14	---	0.0	0.0	3.2	69.0	100.0	2
yellow DA-29-94	1.6	4.0	6.0	75.6	100.0	-----	6
							
black DA-42-14	---	---	0.0	3.2	64.6	100.0	8
yellow DA-29-276	0.6	1.8	3.6	51.4	98.0	100.0	12
							
black DA-29-284	---	0.0	0.6	16.6	96.8	100.0	14
yellow DA-29-277	1.6	58.4	59.0	95.0	100.0	-----	17
							
black DA-29-265	---	----	0.0	12.6	94.0	100.0	19
yellow DA-29-266	---	----	28.4	82.0	99.0	100.0	22
							
black DA-29-275	---	----	0.0	5.0	70.0	100.0	24
yellow DA-29-271	0.0	0.6	60.0	97.0	100.0	-----	27
							
black DA-29-282	1.4	1.8	2.6	54.0	100.0	-----	29
yellow DA-29-281	2.8	7.0	32.0	69.0	91.0	100.0	31
							
black DA-42-16	---	---	0.0	6.0	83.0	100.0	33
yellow DA-42-15	0.6	1.0	1.6	31.0	88.8	100.0	35
							
black DA-29-285	---	0.0	6.4	90.4	100.0	-----	37
yellow DA-29-270	1.2	3.6	10.0	77.2	97.6	100.0	40
							
black DA-42-11	1.2	1.2	0.8	4.6	87.0	100.0	42
yellow green DA-42-6	0.0	0.6	2.0	18.0	90.0	100.0	46
							
orange DA-29-286	2.0	16.6	22.0	34.0	92.6	100.0	48
white DA-29-269	0.6	4.0	16.4	31.0	94.0	100.0	50
							
orange DA-42-10	0.4	1.6	10.0	62.6	89.6	100.0	52
white DA-29-268	1.2	9.0	18.8	50.0	98.6	100.0	54
							
black DA-29-154	---	0.0	----	5.2	29.2	72.4	56

Table 10 summarizes the temperatures at which the 20, 30, 40, and 100 per cent weight losses occur in nitrogen and in air, as well as the point of inflection of the thermogravimetric curve which corresponds to the onset of thermal degradation.

Table 10

Temperatures of Weight Losses and Points of Inflection for Melt (400°C) and Solution Polymers While Being Heated in Air or in Nitrogen

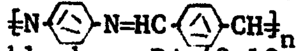
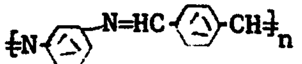
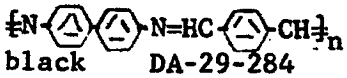
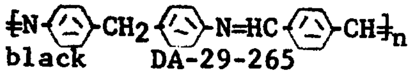
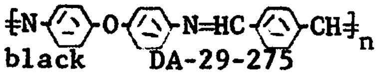
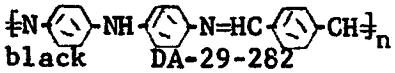
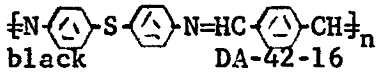
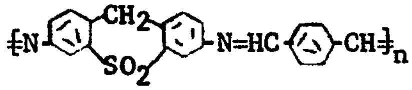
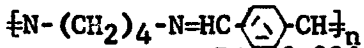
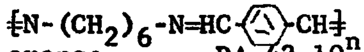
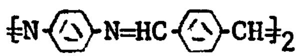
Polymer and Experiment Number	Atm	Temperature °C at Which Weight Loss Occurs				Point of Infl. °C	Appendix Number
		20	30	40	100		
							
black DA-42-13	N_2	730	*			540	1
black DA-42-13	Air	470	476	480	701	480	2
yellow DA-29-94	N_2	500	504	511		450	5
yellow DA-29-94	Air	407	410	413	598	420	6
							
black DA-42-14	N_2	846	*			530	7
black DA-42-14	Air	563	524	580	*	500	8
yellow DA-29-276	N_2	460	487	550	*	425	11
yellow DA-29-276	Air	437	494	498	635	403	12
							
black DA-29-284	N_2	535	545	560	*	530	13
black DA-29-284	Air	510	543	532	615	440	14
yellow DA-29-277	N_2	264	275	285	*	245	16
yellow DA-29-277	Air	248	258	266	518	232	17
							
black DA-29-265	N_2	600	640	*		503	18
black DA-29-265	Air	513	522	530	645	450	19
yellow DA-29-266	N_2	475	481	488	*	460	21
yellow DA-29-266	Air	326	419	447	605	318	22
							
black DA-29-275	N_2	625	1050	*		525	23
black DA-29-275	Air	546	558	566	660	475	24
yellow DA-29-271	N_2	242	286	343		400	26
yellow DA-29-271	Air	378	386	410	550	375	27
							
black DA-29-282	N_2	654	*			520	28
black DA-29-282	Air	478	487	492	598	430	29
yellow DA-29-281	N_2	470	478	488	*	460	30
yellow DA-29-281	Air	285	387	485	620	375	31

Table 10 (cont.)

Temperatures of Weight Losses and Points of Inflection for Melt (400°C) and Solution Polymers While Being Heated in Air or in Nitrogen

Polymer and Experiment Number	Atm	Temperature °C at Which Weight Loss Occurs				Point of Infl. °C	Appendix Number
		20	30	40	100		
							
black DA-42-16	N_2	670	995	*		522	32
black DA-42-16	Air	453	458	466	682	475	33
yellow DA-42-15	N_2	515	522	541	*	490	34
yellow DA-42-15	Air	440	490	525	687	428	35
							
black DA-29-285	N_2	745	*			525	36
black DA-29-285	Air	528	538	546	645	475	37
yellow DA-29-270	N_2	495	507	516	*	300	39
yellow DA-29-270	Air	403	407	410	635	280	40
							
black DA-42-11	N_2	792	*			500	41
black DA-42-11	Air	540	545	550	682	490	42
yellow green DA-42-6	N_2	513	554	630	614	400	45
yellow green DA-42-6	Air	508	518	522	673	400	46
							
orange DA-29-286	N_2	415	428	452	*	320	47
orange DA-29-286	Air	362	370	523	645	250	48
white DA-29-269	N_2	302	390	462	*	235	49
white DA-29-269	Air	352	417	520	635	225	50
							
orange DA-42-10	N_2	410	444	474	673	300	51
orange DA-42-10	Air	462	475	482	664	250	52
white DA-29-268	N_2	400	436	460	*	275	53
white DA-29-268	Air	408	436	460	635	240	54
							
black DA-29-154	N_2	1165	*			550	55
black DA-29-154	Air	410	534	590	783	480	56

* The maximum loss occurred at some value below the per cent indicated by the asterisk.

For values consult the specific thermograms and Tables 8 and 9.

B. Polymers Postheated to 600°C.

Tables 11, 12 and 13 summarize the data obtained from the thermoanalyses of the three selected polymers which were postheated to 600°C. The thermograms obtained for the polymers evaluated are given under the appendix number in the tables. The thermal behavior of the H600 polymer when heated in nitrogen is given in Table 11 and in air in Table 12. Table 13 summarizes the temperatures at which the 20, 30, 40, and 100 per cent weight losses occur in nitrogen and in air, as well as the point of inflection of the thermogravimetric curve which corresponds to the onset of degradation.

Table 11

Per Cent Weight Losses of H600 Polymers While Being Heated in Nitrogen

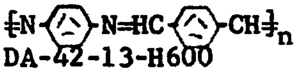
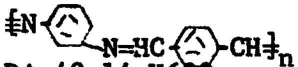
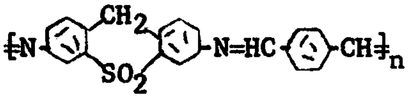
Polymer and Experiment Number	Per Cent Weight Loss at °C											Curve No.1 Appen. No.
	200	300	400	500	600	700	800	900	1000	1100	1176	
 DA-42-13-H600	0.6	1.0	1.6	1.8	2.0	4.0	7.2	8.8	10.0	12.0	14.4	3
 DA-42-14-H600	---	---	0.4	0.6	1.0	3.2	7.0	8.8	10.2	12.6	15.0	9
 DA-42-11-H600	1.8	2.0	2.0	2.4	2.8	4.8	9.4	12.2	13.8	14.6	18.0	43

Table 12

Per Cent Weight Losses of H600 Polymers While Being Heated in Air

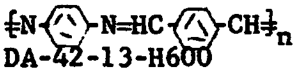
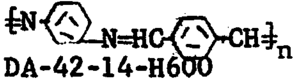
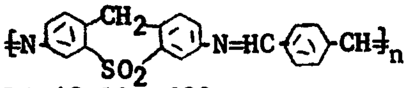
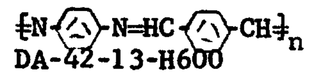
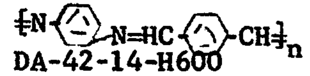
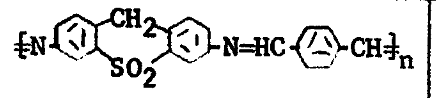
Polymer and Experiment Number	Temperature °C at Which % Weight Loss Occurs						Appendix Number
	200	300	400	500	600	700	
 DA-42-13-H600	---	---	0.0	1.6	70.5	98.0	4
 DA-42-14-H600	---	---	0.0	0.8	58.0	100.0	10
 DA-42-11-H600	3.6	4.0	4.0	6.0	68.0	100.0	44

Table 13

Temperatures of % Weight Losses and Points of Inflection for H600 Polymers in Nitrogen and in Air

Polymer and Experiment Number	Atm	Temp. °C at Which % Weight Loss Occurs				Point of Infl. °C	Appendix Number
		20	30	40	100		
 DA-42-13-H600	N_2	*	*	*	*	630	3
DA-42-13-H600	Air	570	577	582	654	535	4
 DA-42-14-H600	N_2	*	*	*	*	645	9
DA-42-14-H600	Air	571	580	588	701	550	10
 DA-42-11-H600	N_2	*	*	*	*	600	43
DA-42-11-H600	Air	563	579	586	659	525	44

* In all cases the maximum loss was less than 20% even at 1176°C. For specific values consult Table 11 and the specific thermogram.

C. Polymers Postheated to 1176°C.

1. In Nitrogen.

Postheating of the polymers to temperatures much higher than 600°C was accomplished by use of the thermogravimetric analyzer. The finely divided 10 mg. sample was inserted in the apparatus and the sample heated at the rate of 15°C per minute in a nitrogen atmosphere at a flow rate of one (1) standard liter per minute. The heating was continued to the limit of the apparatus, recorded as 1200°C which, corrected for the non-linearity of the thermocouple, is 1176°C.

2. Recycled in Nitrogen.

The selected polymers which were heated in nitrogen to 1176°C were considered for the purposes of these studies, as fully condensed. Accordingly, the samples after this first heating to 1176°C were thermoanalyzed in nitrogen by the simple expedient of allowing the sample and the equipment to cool to room temperature, and recycling the polymer in the equipment under the standard flow of nitrogen. The polymers so treated are designated by the appendix R added to the experiment number. Thus, Experiment DA-42-13-R describes the thermal behavior in nitrogen of polymer DA-42-13, which has been postheated once to 1176°C, and DA-42-13-H600-R that of DA-42-13-H600, which has been postheated once to 1176°C.

3. Recycle in Air.

To contrast the thermal behavior in air of polymers heat-treated to 1176°C with those prepared at 400°C and 600°C the polymer samples which had been subjected to 1176°C in nitrogen 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 and those which had been recycled under nitrogen. In the interest of economy of time, the thermoanalyses 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.

These polymers are designated by appending the letter a to the experiment number of the polymer which has been recycled in nitrogen. Thus, DA-42-13-R-a describes the thermal behavior in air of polymer DA-42-13-R which has been heated twice in nitrogen to 1176°C.

Table 14 lists the appendix number of the thermograms of the polymers which were postheated to 1176°C. In these thermograms, curve 1 plots the data obtained when the polymer was heated to 1176°C, curve 2 describes the thermal behavior of the polymer of curve 1 recycled in nitrogen to 1176°C, and curve 3 plots the data obtained when the polymer of curve 2 was recycled in air.

Table 15 lists the per cent weight loss at 1176°C of the polymers when recycled in nitrogen to a temperature of 1176°C. All polymers showed final

Table 14

Polymers Thermoanalyzed in Nitrogen to 1176°C, Recycled in Nitrogen to 1176°C, Followed by Recycle in Air

Thermogram Appendix No.	Run in Nitrogen Curve No. 1	Recycled in Nitrogen Curve No. 2	Recycled in Air Curve No. 3
1	DA-42-13	DA-42-13-R	DA-42-13-R-a
3	DA-42-13-H600	DA-42-13-H600-R	DA-42-13-H600-R-a
7	DA-42-14	DA-42-14-R	DA-42-14-R-a
9	DA-42-14-H600	DA-42-14-H600-R	DA-42-14-H600-R-a
15	DA-29-284	DA-29-284-R	DA-29-284-R-a
20	DA-29-265	DA-29-265-R	DA-29-265-R-a
25	DA-29-275	DA-29-275-R	DA-29-275-R-a
28	DA-29-282	DA-29-282-R	DA-29-282-R-a
32	DA-42-16	DA-42-16-R	DA-42-16-R-a
38	DA-29-285	DA-29-285-R	DA-29-285-R-a
41	DA-42-11	DA-42-11-R	DA-42-11-R-a
43	DA-42-11-H600	DA-42-11-H600-R	DA-42-11-H600-R-a
55	DA-29-154	DA-29-154-R	DA-29-154-R-a

weight losses of less than 5%, most of which occurred after the polymers had reached temperatures of the order of about 1000°C. The slope of these weight loss curves is very small and none of the curves shows a marked inflection point.

Table 16 summarizes the behavior of the recycled polymers when heated in air, giving the temperature at which weight loss begins, the inflection temperature, the temperature at which a 20% weight loss occurs, and the temperature at which the polymer has completely disappeared as a result of oxidation.

Table 15

Per cent Weight Loss at 1176°C of Polymer Recycled in Nitrogen

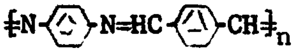
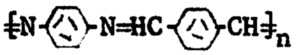
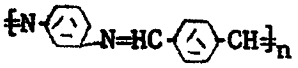
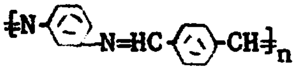
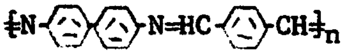
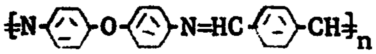
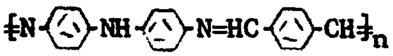
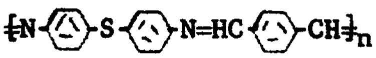
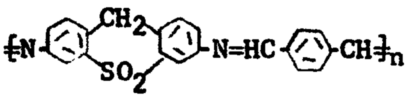
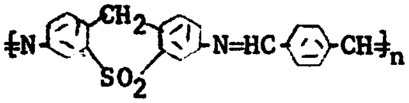
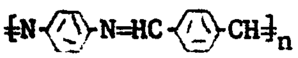
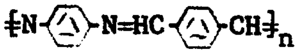
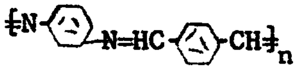
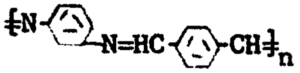
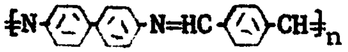
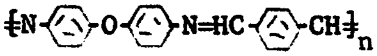
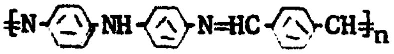
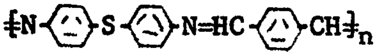
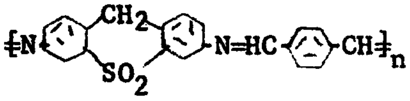
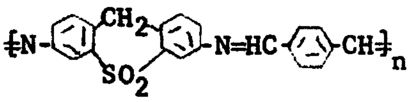
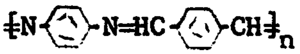
Polymer	% Loss at 1176°C	Experiment No.	Appen. No.	Curve No.
	4.2	DA-42-13-R	1	2
	2.4	DA-42-13-H600-R	3	2
	2.6	DA-42-14-R	7	2
	4.0	DA-42-14-H600-R	9	2
	2.6	DA-29-284-R	15	2
	2.4	DA-29-265-R	20	2
	3.0	DA-29-275-R	25	2
	2.8	DA-29-282-R	28	2
	4.0	DA-42-16-R	32	2
	4.4	DA-29-285-R	38	2
	2.8	DA-42-11-R	41	2
	2.8	DA-42-11-H600-R	43	2
	2.8	DA-29-154-R	55	2

Table 16

Temperatures at Which Weight Loss Begins, Has Occurred to 20%, is Complete When Polymers are Heated in Air After Being Heated to 1176°C in Nitrogen

Polymer	Experiment Number	Sample Begins to Lose Wt. at °C	20% Wt. Loss at °C	Sample disappears at °C	Infl. Point
	DA-42-13-R-a	510	565	800	550
	DA-42-13-H600-R-a	600	660	1000	600
	DA-42-14-R-a	430	560	700	450
	DA-42-14-H600-R-a	550	620	830	565
	DA-29-284-R-a	520	650	800	550
	DA-29-265-R-a	450	590	660	480
	DA-29-275-R-a	520	620	860	550
	DA-29-282-R-a	550	660	900	578
	DA-42-16-R-a	420	530	740	490
	DA-29-285-R-a	480	620	900	560
	DA-42-11-R-a	475	620	720	525
	DA-42-11-H600-R-a	500	630	860	580
	DA-29-154-R-a	480	580	660	545

D. General Discussion.

The data of the thermograms show that

1. The polycondensations performed to a temperature of 400°C are not complete. This is indicated by the losses in weight in nitrogen of these polymers compared to the much lower losses found in polymers condensed to higher temperatures, such as to 600°C and to 1176°C. This observation confirms earlier data,[1,2] as well as the results of recent studies[3] involving the acetal exchange syntheses of the polymers.
2. The thermal stabilities in nitrogen and in air of the black conjugated and pseudoconjugated polymers prepared by the melt bis-exchange reaction are much higher than the stabilities of the corresponding yellow-type brick-dust polymers prepared in solution.
3. The thermal stabilities in nitrogen and in air of the aliphatic-type non-conjugated Schiff-base polymer prepared either by the melt bis-exchange reaction in solution are much lower than the conjugated and pseudoconjugated polymeric Schiff bases.
4. The differences in the thermal stabilities of the aliphatic-type Schiff base polymers prepared by melt Schiff base exchange and by solution methods are small. This contrasts with the data on the conjugated and pseudoconjugated Schiff base polymers and is attributed to the fact that the polymerization condensation of the aliphatic-type polymers is homogeneous in both melt and solution systems, whereas, in the aromatic type the condensation is homogeneous in the melt bis-exchange system and heterogeneous in the solution system.
5. The thermal stabilities of the aliphatic-type Schiff bases studied, $\left[N-(CH_2)_4-N{=}HC-C_6H_4-CH\right]_n$ and $\left[N-(CH_2)_6-N{=}HC-C_6H_4-CH\right]_n$ are surprisingly

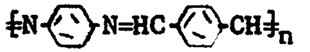
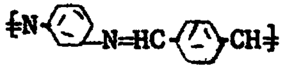
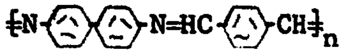
good; of the order of 250°C in nitrogen and in air. They undergo decomposition in nitrogen and in air in the region of 300°C to 350°C.

6. The thermal stabilities can be compared generally in a number of ways such as from 1) the weight losses at specific temperatures, 2) the temperatures at which specific weight losses occur, or 3) their decomposition temperature as indicated by points of inflection in the weight-temperature thermogravimetric plots. On this basis, a number of observations can be made concerning the thermal stability of the conjugated and pseudoconjugated polymers condensed to 400°C.

a. Thermal Stability in Nitrogen of Polymers Condensed to 400°C.

i. The thermal stabilities of all the polymers in nitrogen below the inflection point is very good and within the range of 500-550°C.

ii. The completely conjugated polymers show the best general overall thermal stability in nitrogen as judged from the inflection point and total weight loss at 1000°C and 1176°C.

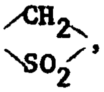
Polymer	Exper. No.	Appen. No.	Infl. Point	% Wt. Loss at	
				1000°C	1176°C
	DA-42-13	1	540	24.4	29.4
	DA-29-154	55	550	14.4	20.4
	DA-42-14	7	540	21.6	28.6
	DA-29-284	13	530	55.0	58.0

At high temperatures, the polymer containing the diphenyl moiety, DA-29-284, shows less stability than would be expected. The anomaly cannot be explained at this time.

iii. There is no substantial difference in the thermal stability in nitrogen of the polymers prepared from the dibenzylidene derivatives of para-phenylenediamine and meta-phenylenediamine.

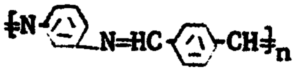
Since the cost of meta-phenylenediamine is lower than the para compounds, its use is preferred and recommended.

iv. The effect of thermal stability in nitrogen of the polymers resulting from changes in conjugation of the polymers is not as great as would be expected in the case of those polymers which are pseudoconjugated, that is, polymers of the structure, $\left[N\text{-}Ar\text{-}X\text{-}Ar\text{-}N{=}HC\text{-}Ar\text{-}CH \right]_n$, in which the conjugation is not completely inhibited by a X bridge between the aromatic rings.

The pseudoconjugated polymers in which the bridges are $-CH_2-$, $-O-$, $-NH-$, $-S-$, $-SO_2-$, and  $\left\langle \genfrac{}{}{0pt}{}{CH_2}{SO_2} \right\rangle$ have inflection points of the order of 25-50°C lower in temperature than those of the conjugated polymers; and their weight losses in the range of 600°C to 1000°C are about 0-50% higher than those of the conjugated polymers. The greatest loss at 1000°C is shown by the polymer containing the $-CH_2-$ bridge. The weight losses in nitrogen of the pseudoconjugated polymer in increasing order of stability at 1000°C for the various X bridges are: $-CH_2-$, 37.6%; $-S-$, 30.0%; $-NH-$, 28.8%;  $\left\langle \genfrac{}{}{0pt}{}{CH_2}{SO_2} \right\rangle$, 28.6%; $-SO_2-$, 24.6%.

v. The thermogravimetric analytical data obtained on the pseudoconjugated polymers which were prepared under arbitrarily selected polymerization conditions indicate a good possibility that the thermal properties of these polymers for use in a nitrogen or other inert atmosphere can be developed to approximate those of the conjugated polymers.

b. Thermal Stability in Air of Polymers Condensed to 400°C.

i. When the conjugated and pseudoconjugated polymers are condensed to a temperature of 400°C, the heat-resistance of the polymers in air lies in the range of 430-500°C. The best heat-resistance is shown by conjugated polymers, $\{N-C_6H_4-N{=}HC-C_6H_4-CH\}_n$, DA-42-13, DA-42-14, and DA-29-154 with the meta diamine polymer,  having the highest value of 500°C. Of the pseudoconjugated polymers, the oxygen polymer, $\{N-C_6H_4-O-C_6H_4-N{=}HC-C_6H_4-CH\}_n$, DA-29-275, shows the highest resistance in air with a temperature of inflection of 475°C. In fact, its weight loss in air at 600°C of 70% compares favorably with the values of 69% and 64% for the conjugated polymers, DA-42-13 and DA-42-14, respectively.

The indication that the polymerization is not completed at 400°C is found in the difference of the thermoanalyses of the polymers $\{N-C_6H_4-N{=}HC-C_6H_4-CH\}_n$, DA-42-13 and DA-29-154, in which the former was condensed to 400°C and the latter to 450°C. At 600°C in air, the per cent weight loss of DA-42-13 is 69% and of DA-29-154 is 39.2%. These data indicate the possibility of achieving greater thermal stability in the Schiff base polymers is continuing the condensation to temperatures higher than 400°C and under condition of time, temperature and pressure determined independently for the specific polymer to be synthesized.

ii. The thermal stability of the aliphatic-type non-conjugated Schiff bases in air is relatively poor and of the order of 250°C, losing about 20% of their weight by 400°C.

7. When the condensation of the polymers is performed to a temperature of 600°C a number of effects due to the heating to this temperature are noted. It can be concluded from the nature of the weight-

temperature curves of the polymers thermoanalyzed in nitrogen, that twenty minutes heating time at 600°C is insufficient to cause complete condensation in the polymers. The thermograms indicate that polycondensation, and possibly other types of condensations continue to 1176°C.

a. Thermal Stability in Nitrogen of Polymers Condensed to 600°C.

i. The thermograms of the polymers, DA-42-13-H600, DA-42-14-H600 and DA-42-11-H600, condensed to a temperature of 600°C, clearly show that their stabilities in nitrogen are greatly increased over the same polymers condensed to 400°C. All the H600 polymers show losses of less than 20% of their weight at 1176°C. The two phenylenediamine polymers, DA-42-13-H600 and DA-42-14-H600 lose only about 15% of their weight at 1176°C, about 10% at 1000°C, and about 5% at 750°C. Based on inflection points, the thermal stability in nitrogen of these three polymers are DA-42-13-H600, 630°C; DA-42-14-H600, 645°C; and DA-42-11-H600, 550°C.

ii. In the thermograms of these three H600 polymers (appendix numbers 3, 9, and 43), 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 400°C, the first negative slope is found approximately in the 500-600°C region; in those postheated to 600°C it is found in the region of 700°C.

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 gasses 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 760-800°C. This will require metal heating blocks capable of withstanding these temperatures; for this purpose, copper, M.P. >

1000°C, may be satisfactory. It would also require a new design or structure in the means of heating the 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 polymers, when heated in nitrogen to 1176°C, also became black but they retained a brick-dust character.

b. Thermal Stability in Air of Polymers Condensed to 600°C.

The thermal stabilities in air of the polymers condensed to 600°C are higher than the values found for the same polymers condensed to 400°C. For example, the thermal stability, as based on inflection points, in air for the polymer DA-42-13-H600 is 535°C compared to 480°C for DA-42-13; for DA-42-14-H600 it is 550°C compared to 500°C for DA-42-14; and for DA-42-11-H600 it is 525°C compared to 490°C for DA-42-11.

8. Thermal Stabilities of Polymers Condensed to 1176°C.

a. In Nitrogen.

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 as indicated by the substantially horizontal linear plots of weight versus temperature in each curve 2 of the thermograms of appendix numbers 1, 3, 7, 9, 15, 20, 25, 28, 32, 38, 41, 43, and 55. The weight losses vary from 2.4 to 4.4% in the thirteen polymers studied.

This means that by pretreating the polymers in an inert atmosphere at temperatures in excess of 800°C, for example, in the region of 1000°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 high purity helium as the inert atmosphere relative to nitrogen, and to perform some of the thermograms at reduced pressures.

b. In Air.

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 1, 3, 7, 9, 15, 20, 25, 28, 32, 41, 43, and 45, all showed heat stabilities in air in excess of 480°C with a spread in temperature range of 480-600°C. Polymer DA-42-13-H600-R (Appendix No. 31) showed stability to 600°C (1112°F) in air.

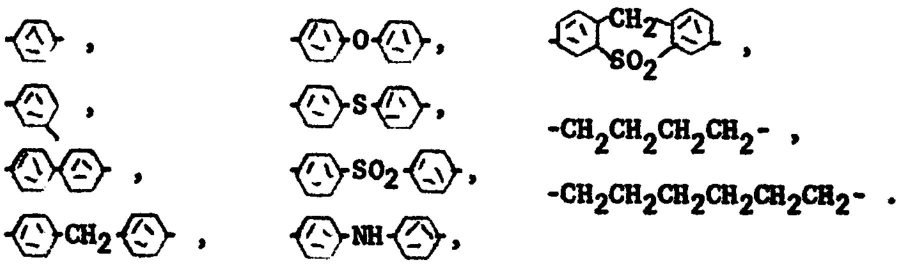
9. When the polymers are meant for use in air, condensation to a temperature of about 600°C, or to some slightly higher temperature to be chosen after more studies, appears to be satisfactory. Whereas, if the polymers are intended for use in an inert atmosphere to temperatures in excess of 600°C, the polycondensation should be performed to temperatures of the order of 1000°C or higher.

VI. Summary and Conclusions.

1. Three new bis-Schiff base monomers have been synthesized completing the series of eleven (11) monomers containing representative conjugated, pseudoconjugated and non-conjugated structures. The con-

tinuous azeotrope method[1,2] was successfully applied in these syntheses.

2. Eleven polymers containing conjugated, pseudoconjugated and non-conjugated moieties in their backbone structures were prepared. They can be represented by the general formula, , wherein -Z- represents



$-CH_2CH_2CH_2CH_2-$,

$-CH_2CH_2CH_2CH_2CH_2CH_2-$.

In these polymers the dialdehyde moiety,  was maintained constant.

3. The eleven polymers were synthesized in duplicate by two methods:[1,2] a) the bis-Schiff base exchange melt process, and b) the solution method. By the solution method, the conjugated and pseudoconjugated polymers were obtained as yellow-type brick-dust polymers. The same polymer prepared by the melt bis-Schiff exchange process were black, glossy polymers in all cases which, during synthesis, passed through a fusible, viscous, fabricable stage changing in color progressively from yellow to orange to brown to black, confirming the broad applicability of this reaction and process. As was expected, the non- conjugated polymers containing the aliphatic bridges, $\text{-}(CH_2)_4\text{-}$ and $\text{-}(CH_2)_6\text{-}$ were very light in color, when prepared by either the melt bis-exchange or the solution process, giving evidence of substantial inhibition of the conjugation in their linear structures.

4. The melt bis-exchange conjugated and pseudoconjugated polymers were prepared under identical conditions selected on the basis of limited preliminary experiments. These conditions are referred to as

"standardized conditions" in which the condensation is performed to a maximum temperature of 400°C. These conditions were found to be too severe for the synthesis of the non-conjugated aliphatic-type Schiff base polymers, for which 250°C was the maximum temperature used in the polycondensation; at this temperature, some decomposition, as evidenced by change in color of the polymer from white to orange, is noted.

5. Three exploratory polymerizations were performed with the intention of by-passing the syntheses of the bis-Schiff base monomers. These polymerizations involved the direct use of the two amines, and the two aldehydes, which constitute the monomers. A black polymer, which passed through the fusible stage, was obtained by the direct melt polymerization of m-phenylenediamine, aniline, terephthaldehyde and benzaldehyde. This reaction warrants further study.

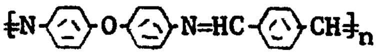
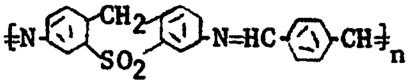
6. Thermovravimetric analyses performed on the polymers clearly show that the polymers prepared by the bis-exchange reaction have greater thermal resistance than the polymers prepared by solution methods. This difference, however, is lowest in the non-conjugated aliphatic-type Schiff base polymers.

7. The non-conjugated aliphatic-type have much lower heat-resistance than the conjugated and pseudoconjugated Schiff base polymers.

8. Analyses of the thermograms of the conjugated and pseudoconjugated polymers show that the polymers prepared by the melt bis-exchange reaction have very good thermal stabilities.

9. The conjugated and pseudoconjugated polymers condensed to a temperature of 400°C show a heat-resistance in nitrogen of 500-550°C. The conjugated polymers, $\left[N-C_6H_4-N{=}HC-C_6H_4-CH \right]_n$, have the highest values of 540°C and 550°C; the slightly lower values in the range of 500-525°C

for the pseudoconjugated polymers is surprisingly high.

10. The conjugated and pseudoconjugated polymers condensed to 400°C show a heat-resistance in air of 430-500°C. The conjugated polymers, $+N-C_6H_4-N=HC-C_6H_4-CH+_n$, have the highest values with a value for the meta-diamine polymer, $+N-C_6H_4-N=HC-C_6H_4-CH+_n$ of 500°C. The pseudoconjugated polymer, , shows a heat-resistance in air of 475°C.
11. The conjugated polymer, $+N-C_6H_4-N=HC-C_6H_4-CH+_n$ prepared from dibenzylidene-m-phenylenediamine has heat-resistance at least as good as that prepared from the p-phenylenediamine derivative.
12. The non-conjugated aliphatic Schiff-base type polymers show a heat-resistance of about 250°C and decompose in the range of 300-350°C in both nitrogen and in air.
13. The data on the thermograms indicate that the polycondensation is not completed at 400°C and should be continued to at least 600°C.
14. The two conjugated and one pseudoconjugated polymers which were condensed further by postheating the polymers in nitrogen to 600°C show a marked improvement in their stability in nitrogen. The conjugated polymers, $+N-C_6H_4-N=HC-C_6H_4-CH+_n$, showed the highest resistance with values of 630°C for DA-42-13-H600, and 645°C for DA-42-14-H600. The pseudoconjugated polymer,  DA-42-11-H600 has a heat-resistant value of 550°C.
15. The thermal stability in air is also increased in those polymers which were condensed further by postheating to 600°C. The two conjugated polymers, $+N-C_6H_4-N=HC-C_6H_4-CH+_n$, DA-42-13-H600 and DA-42-14-H600 showed heat-resistance in air of 535°C and 550°C respectively, while the pseudoconjugated polymer, DA-42-11-H600,

showed a heat-resistance in air of 525°C.

16. The thermogravimetric analyzer apparatus was used as an instrument to postheat the conjugated and pseudoconjugated polymers in nitrogen to 1176°C to complete the polycondensation. These polymers were considered as fully condensed and their thermal stabilities in nitrogen and in air were evaluated. Judging from the nature of the thermogram curves, the polycondensation appears to continue to the 800-1000°C region. Some other type of condensation may be occurring also in the 800-1176°C region.

17. Polymers condensed to 1176°C (2026°F) show a heat-resistance in nitrogen of about 1176°C (2026°F). The data in the thermograms show only small total losses of the order of two to five per cent. Most or all of these losses occur after about 1000°C as is evident by a slight inflection in the curves. This loss at temperatures above 1000°C may be due to loss of hydrogen resulting from coupling of aromatic rings.

18. Polymers condensed to 1176°C show a heat-resistance in air in the range of 480-600°C. The fully conjugated polymer, DA-42-13-H600-R showed a stability in air of 600°C (1112°F). This appears to be the temperature region in which the combustion of the polymer occurs.

19. When the polymers are meant for use in air a condensation temperature of about 600°C appears to be satisfactory, but if the polymers are intended for use in an inert atmosphere to temperatures in excess of 600°C, the polycondensation should be performed to temperatures of the order of 1000°C or higher.

20. The experimental work detailed in this report points to the need for further study in a number of areas.

VII. Future Research.

1. Establish the best overall conditions for the condensation polymerization of p-xylylidenedianil with dibenzylidene-m-phenylenediamine and dibenzylidene-p-phenylenediamine respectively, within the following reaction parameters.
   a. without and with catalysis
   b. establish temperature range of reaction
   c. establish time limits of reaction.
2. Explore the synthesis of polymers directly in a one-stage melt process from m-phenylenediamine, terephthaldehyde, aniline and benzaldehyde with the following reaction parameters:
   a. with and without catalysis
   b. establish temperature range of reaction
   c. establish time limits of reaction.
3. Establish methods for the determination of the kinetics of the bis-Schiff base exchange polymerization reaction. To date, an unambiguous method for this study has not been established.
4. Synthesize the meta-phthaldehyde, m-C_6H_4-$(CHO)_2$, and evaluate it in the syntheses of para-meta and para-para type polymers by
   a. bis-Schiff exchange reactions and
   b. direct synthesis using the phenylenediamines, the meta-phthaldehyde, aniline, and benzaldehyde.
5. Perform differential thermal analyses (DTA) on representative polymers in this report and the polymers prepared under items 1 to 4 inclusive.
6. Study the postheating to the region of 800-1000°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.

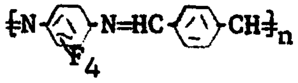
7. Determine best point in the polymerization at which the fusible polymer should be isolated for conversion to infusible condition:
   a. evaluate the use of Lewis acids in the process of conversion to infusibility.

8. Compare nitrogen and helium as the gaseous media in the postheating of polymers to 1176°C and in TGA measurements.

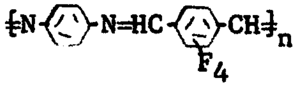
9. Undertake appropriate physical studies involving the following solid state properties of selected polymers and to correlate these properties by
   a. semi-conductor measurements as a function of temperature and conformance to Ohm's law,
   b. EPR measurements as a function of temperature and relationship to the number of "free" electrons to conductivity,
   c. heat capacity measurements as a function of temperature for correlation to conductivity and EPR.

10. Evaluate conjugated perfluoro polymeric Schiff bases in which the hydrogen atoms in the benzene rings have been replaced by fluorine atoms with the expectation of improving the thermal stability of the polymers, especially in air. This study shoud, for comparative purpose, be performed in three stages to produce polymers of the general structure

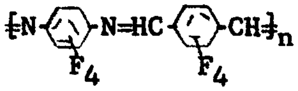
a)



b)



c)



11. Attempt to determine molecular weight of polymers by end-group analysis using perfluoro compounds such as F_5C_6CHO and $F_5C_6NH_2$ as end groups in the bis-Schiff bases, $F_5C_6CH{=}N{-}C_6H_4N{=}HC{-}C_6F_5$, and $F_5C_6N{=}HC{-}C_6H_4{-}CH{=}N{-}C_6F_5$ from which the polymers are prepared.

12. Attempt to determine molecular weight of the polymers by reacting the polymers with various quantities of benzalaniline to reduce the molecular weights to points where colligative properties can be measured. Then apply statistical analysis and computor programming to attempt to solve this problem.

13. Initiate study to evaluate the photoconductivity of the polymers as a function of
    a. wavelength of the incident light,
    b. temperature.

VIII. Acknowledgment.

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

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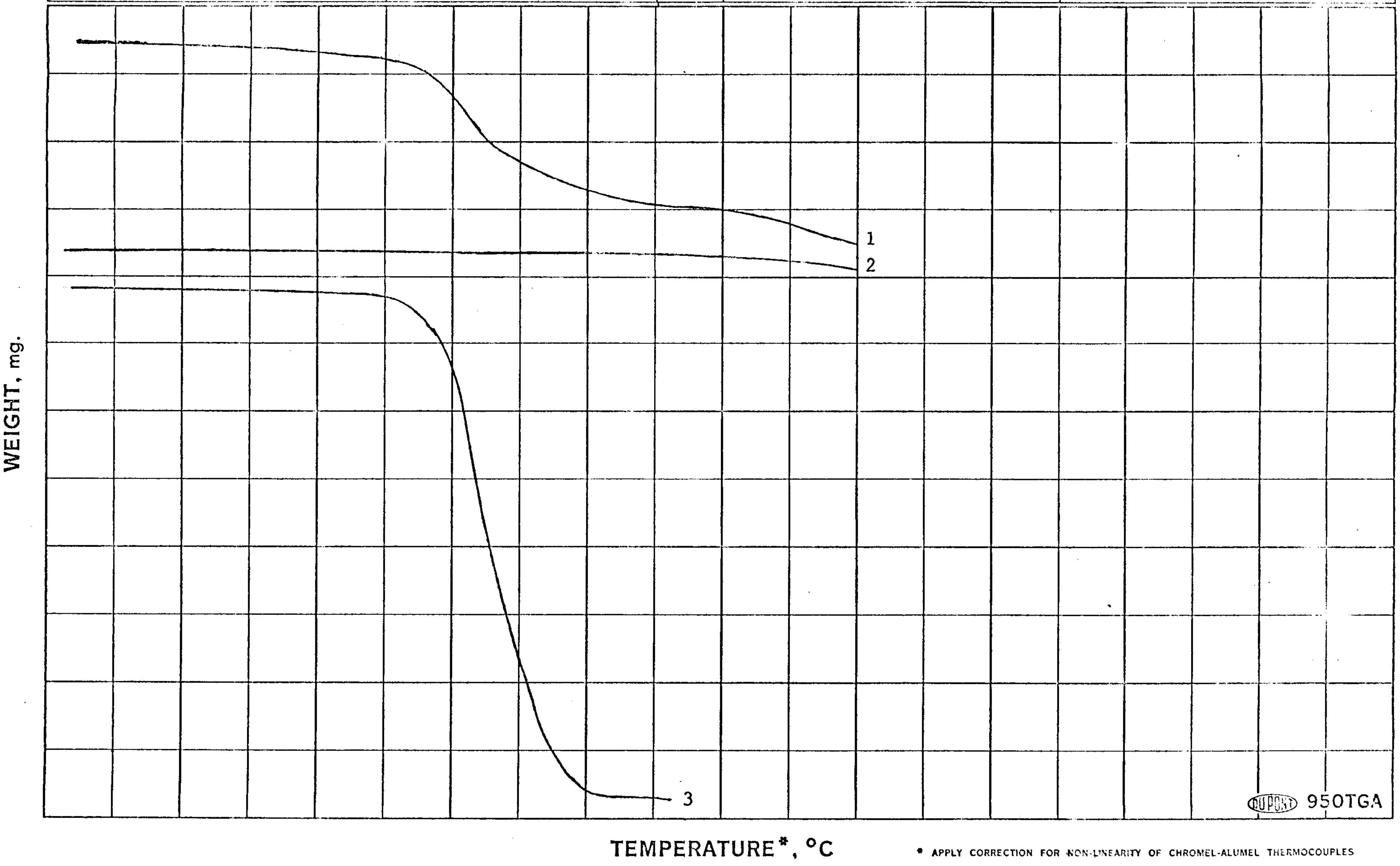
Appendix No.

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-42-13 $\left[N-C_6H_4-N=HC-C_6H_4-CH \right]_n$ 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 9-15-65 OPERATOR JVC HEATING RATE 15 °C/min. ATM. (1) N_2, (2) N_2, (3) air TIME CONSTANT 2 sec.



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

Appendix No. 2

DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-42-13

$\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$

SIZE 9.6 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.

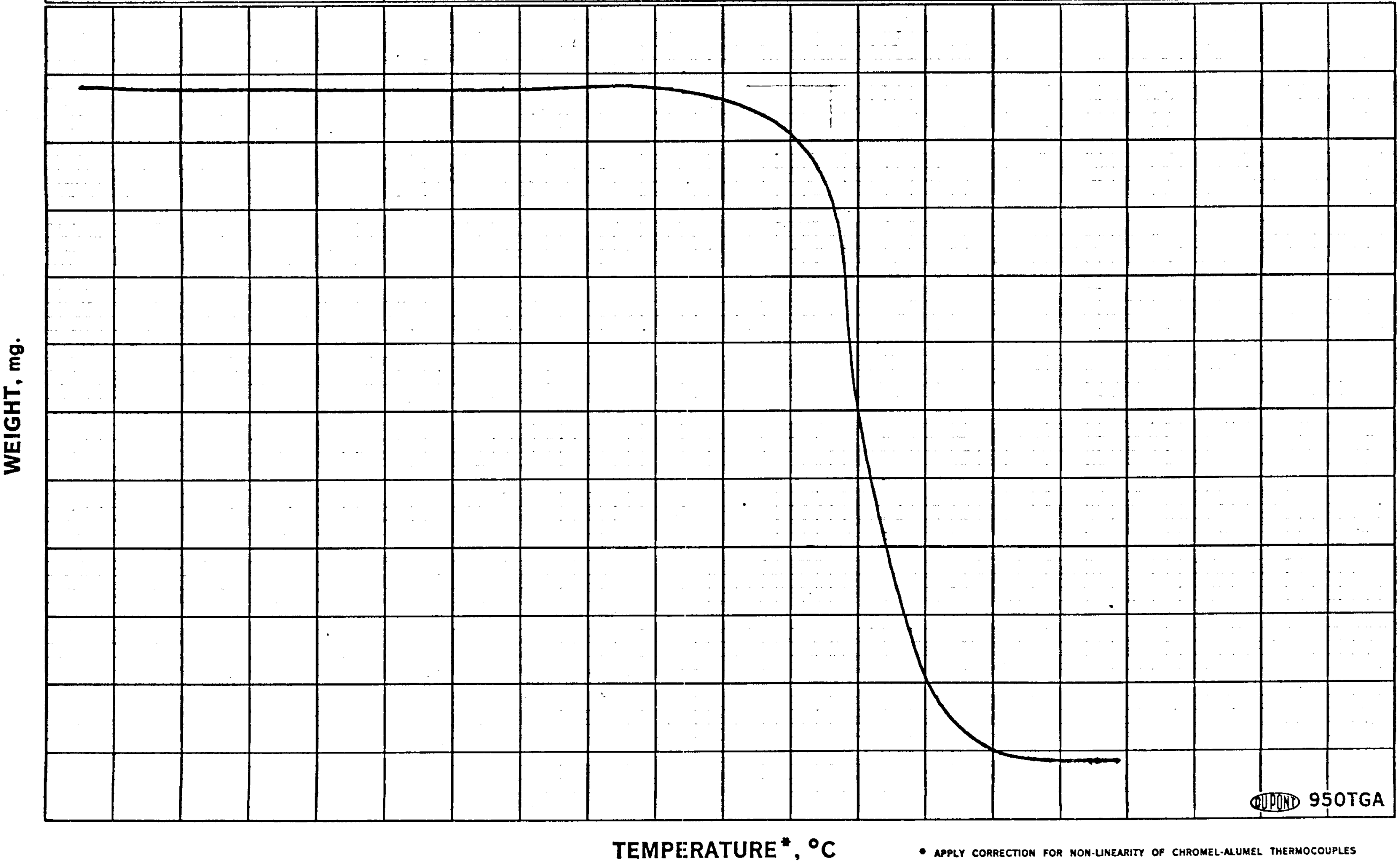
RUN NO. DATE 9-14-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. air

TIME CONSTANT 2 sec.



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

INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-42-13-H600	X-AXIS	Y-AXIS	RUN NO. ______ DATE 9-15-65
$\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR JVC
	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. (1) N_2, (2) 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

Appendix No. 3

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

SAMPLE: DA-42-13-H600

$\{N-C_6H_4-N{=}HC-C_6H_4-CH\}_n$

SIZE 9.2 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.

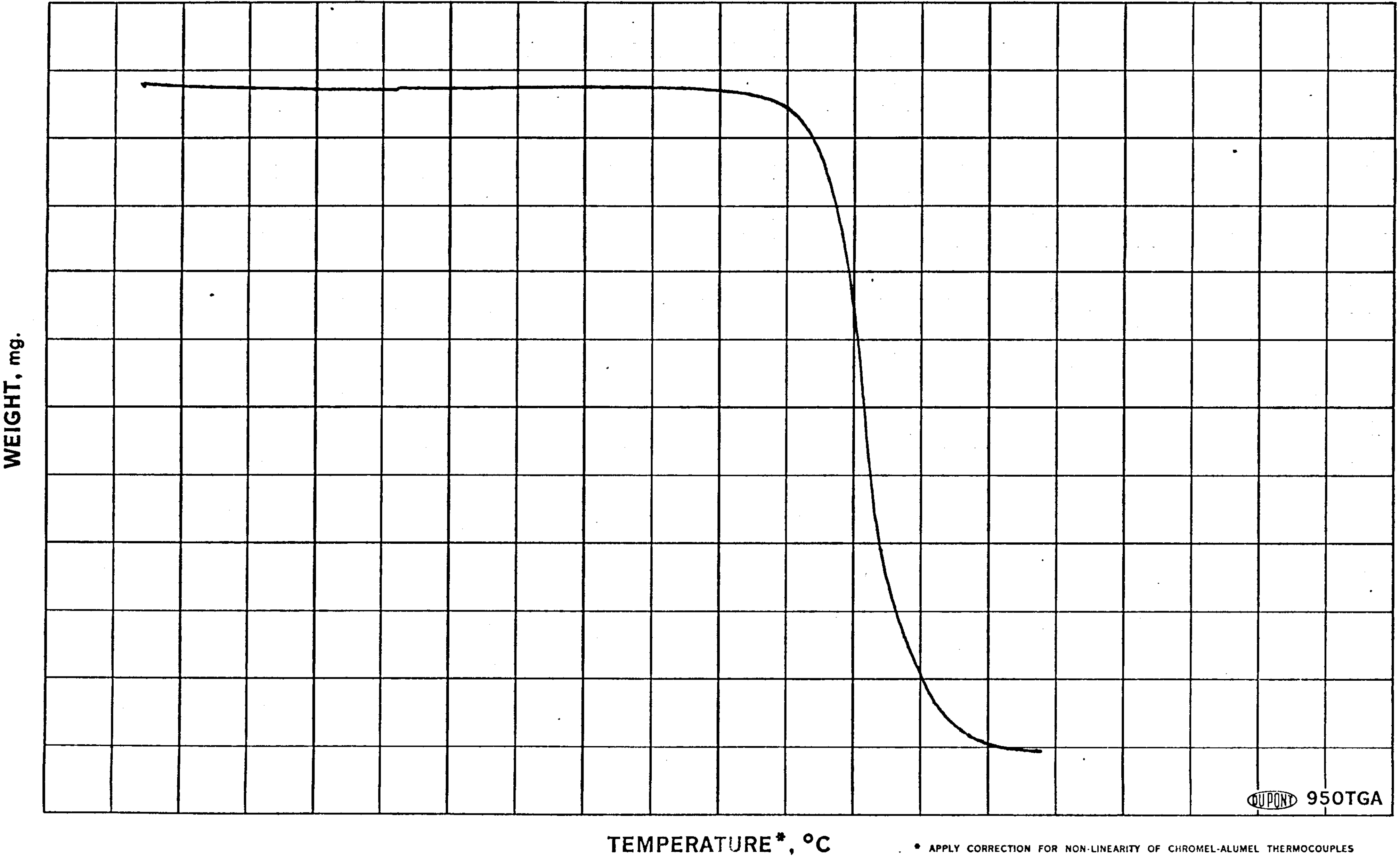
RUN NO. DATE 9-14-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. air

TIME CONSTANT 2 sec.

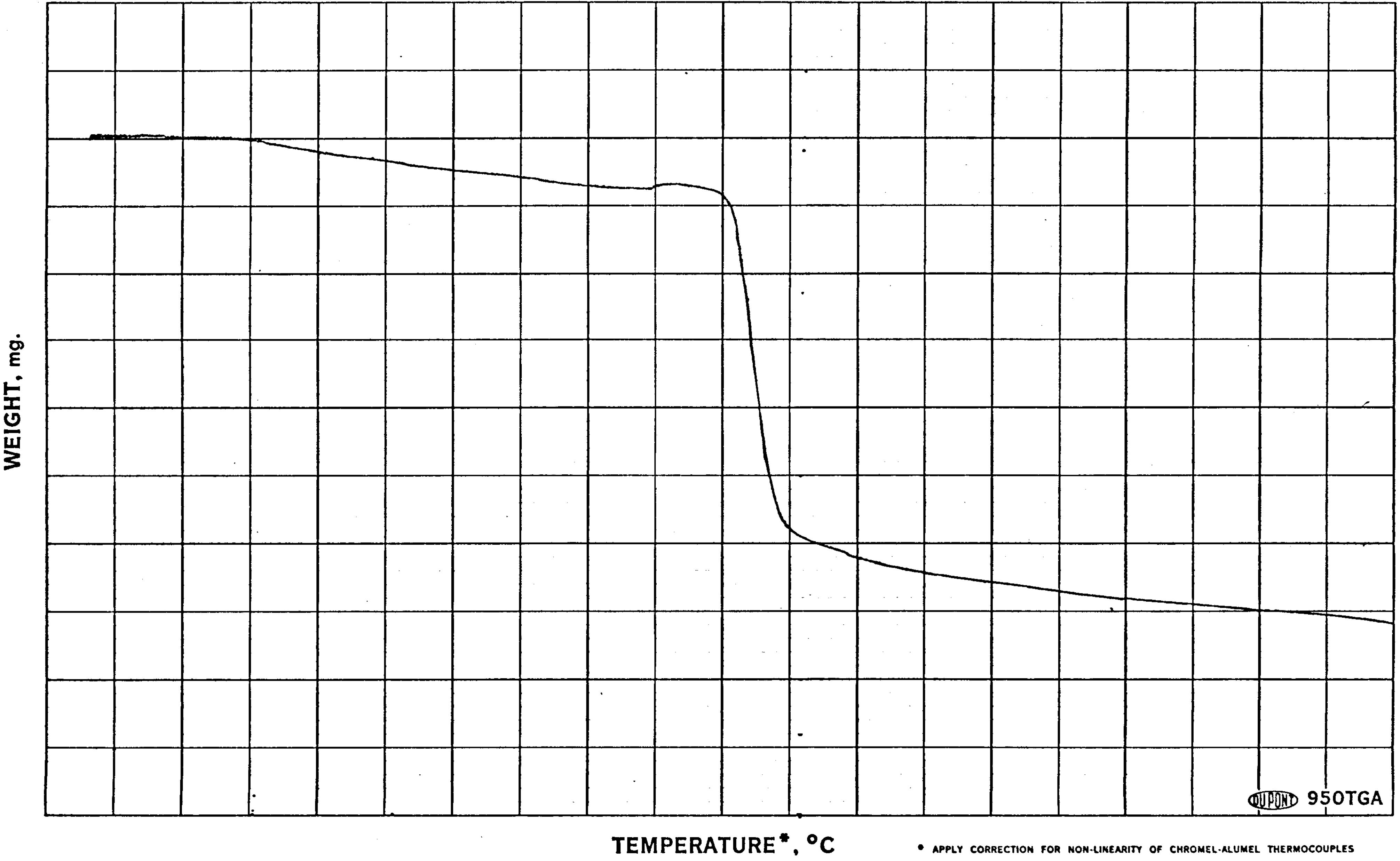


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 4

INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-29-94	X-AXIS	Y-AXIS	RUN NO. ____ DATE 7-9-65
$\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch	OPERATOR JVC
yellow polymer	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 25 °C/min.
			ATM. nitrogen
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. 6

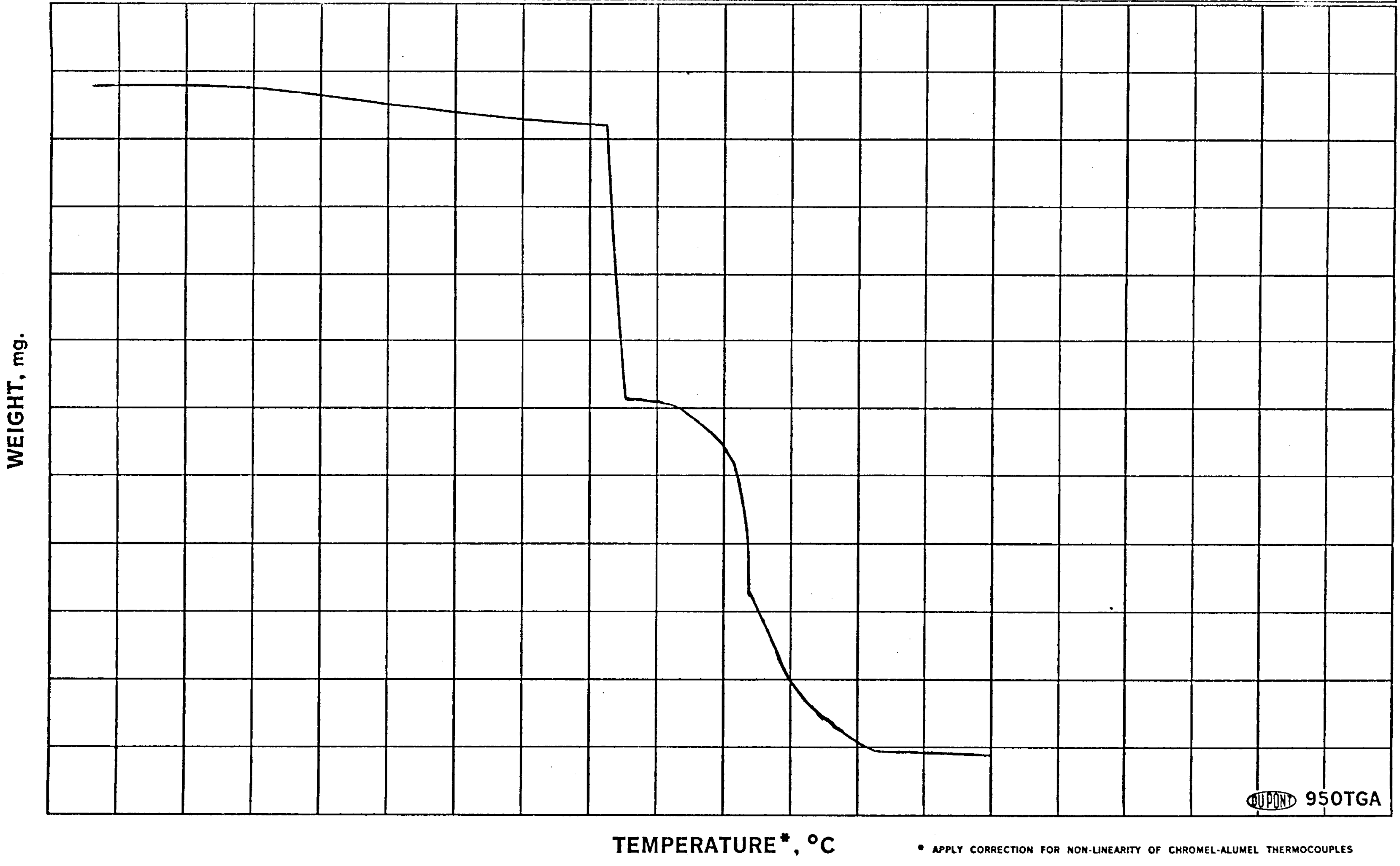
DUPONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-29-94
$[N-C_6H_4-N=HC-C_6H_4-CH]_n$
yellow polymer
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 7-20-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



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

Appendix No. 7

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-42-14

m
$\{N-C_6H_4-N{=}HC-C_6H_4-CH\}_n$

SIZE 10 mg.

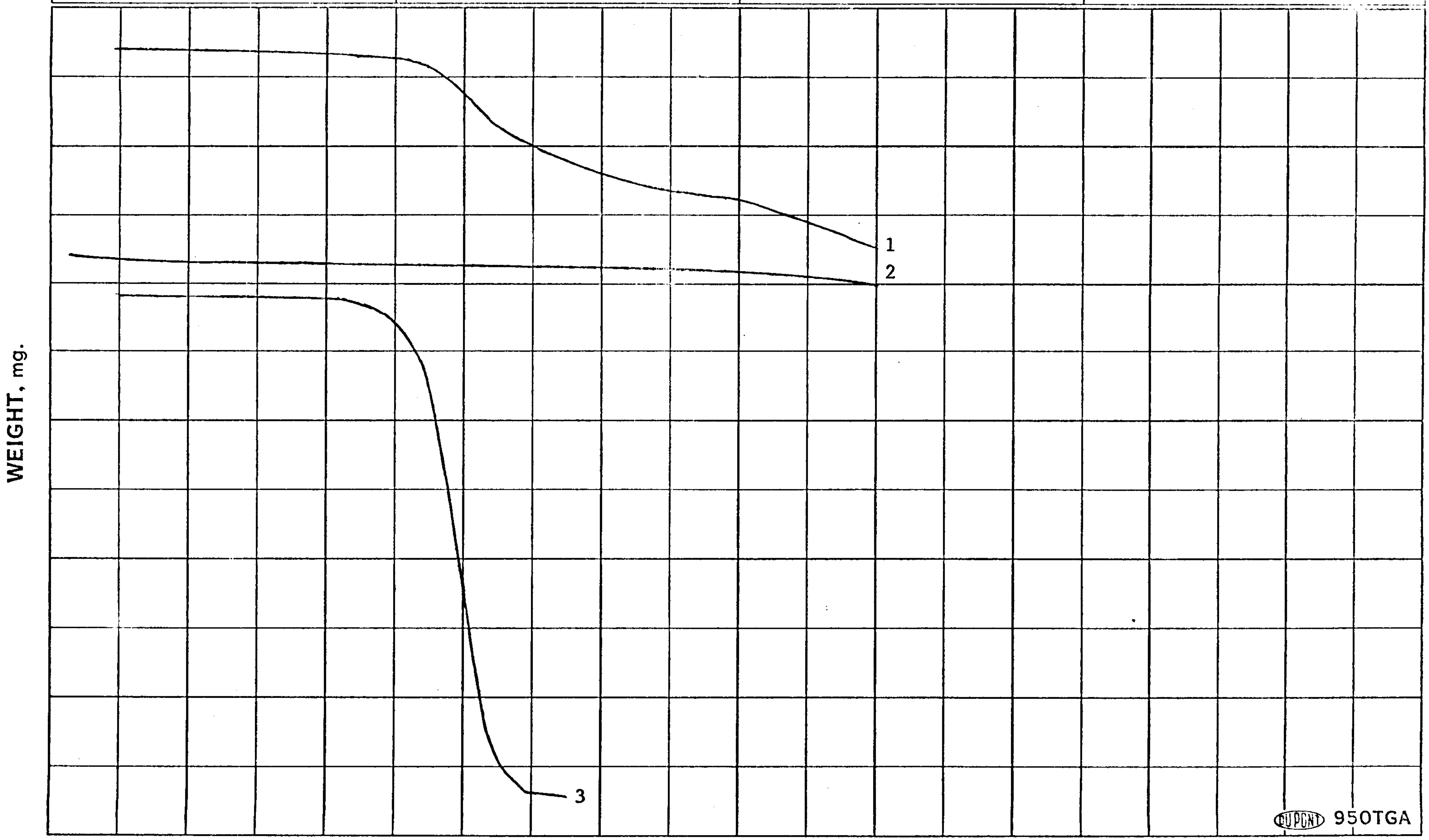
X-AXIS

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 9-29-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. (1) N_2, (2) N_2, (3) air
TIME CONSTANT 2 sec.



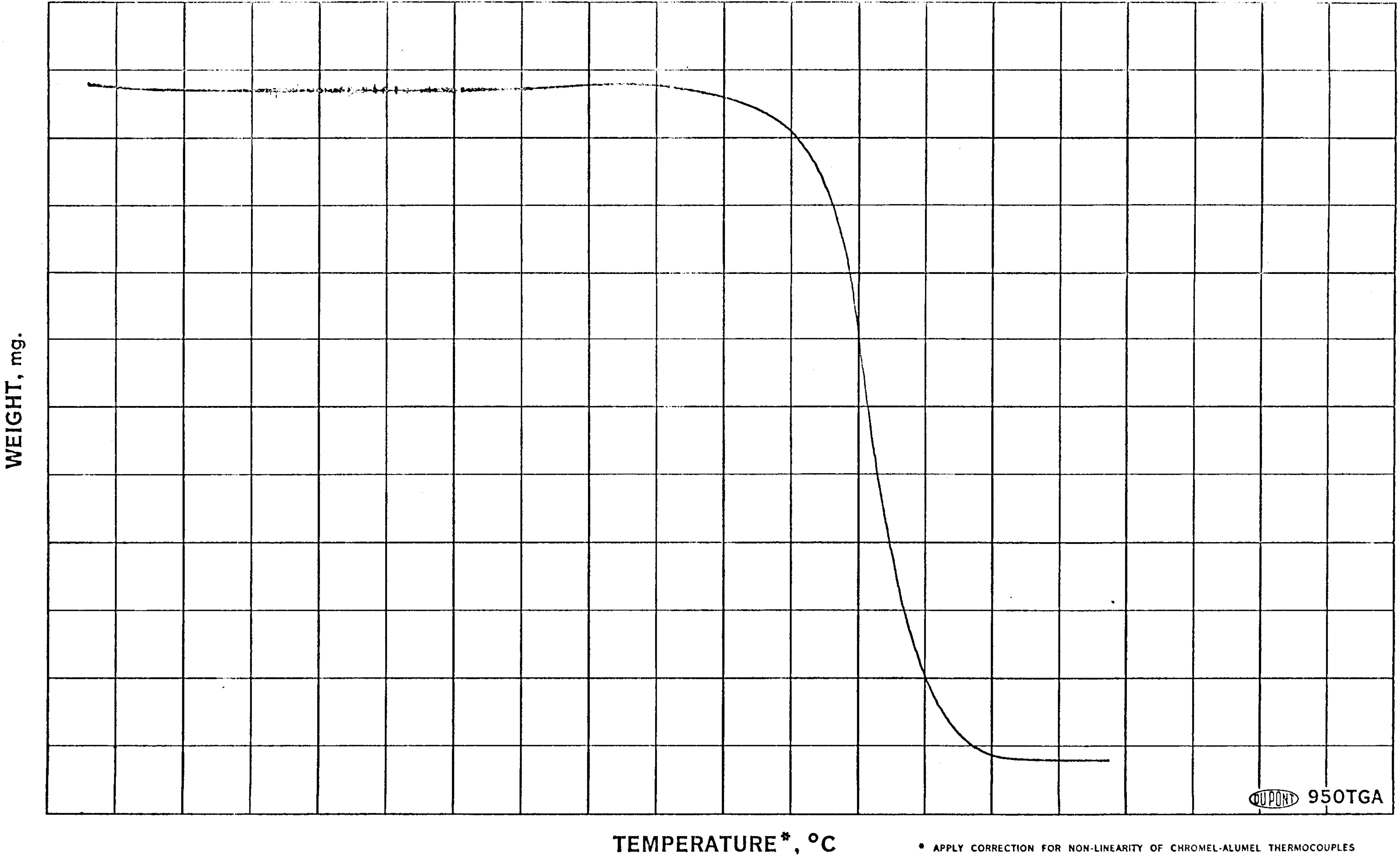
TEMPERATURE*, °C

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

Appendix No. 8

DUPONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-42-14 $\{N-\overset{m}{C_6H_4}-N{=}HC-C_6H_4-CH\}_n$ 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 8-27-65 OPERATOR JVC 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, DELAWARE

SAMPLE: DA-42-14-H600

$\{\overset{m}{N}-C_6H_4-N=HC-C_6H_4-CH\}_n$

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.

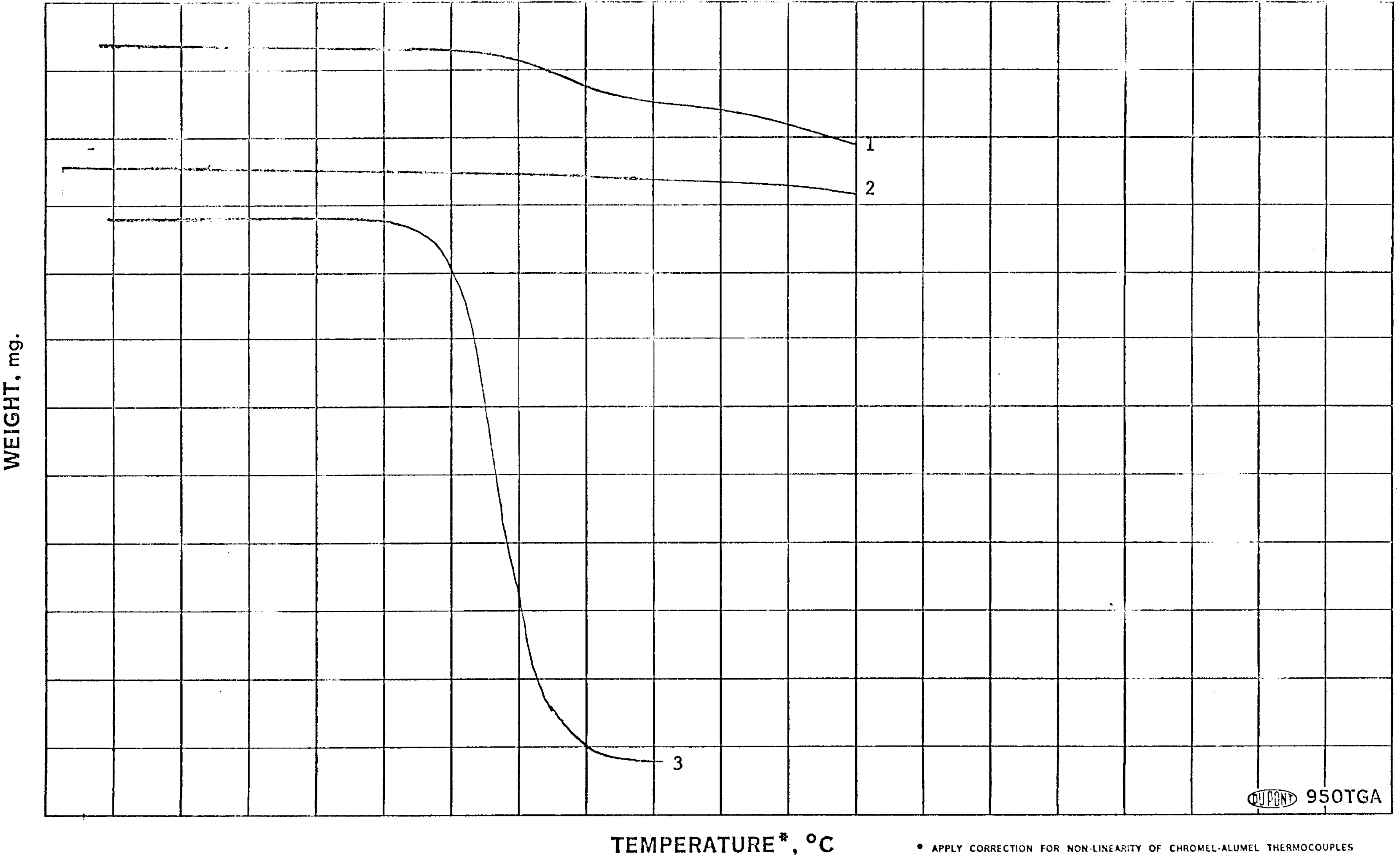
RUN NO. ____ DATE 8-30-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. (1) N_2, (2) N_2, (3) air

TIME CONSTANT 2 sec.



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

INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-42-14-H600

$\{\overset{m}{N}-C_6H_4-N=HC-C_6H_4\cdot CH\}_n$

SIZE 9.9 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.

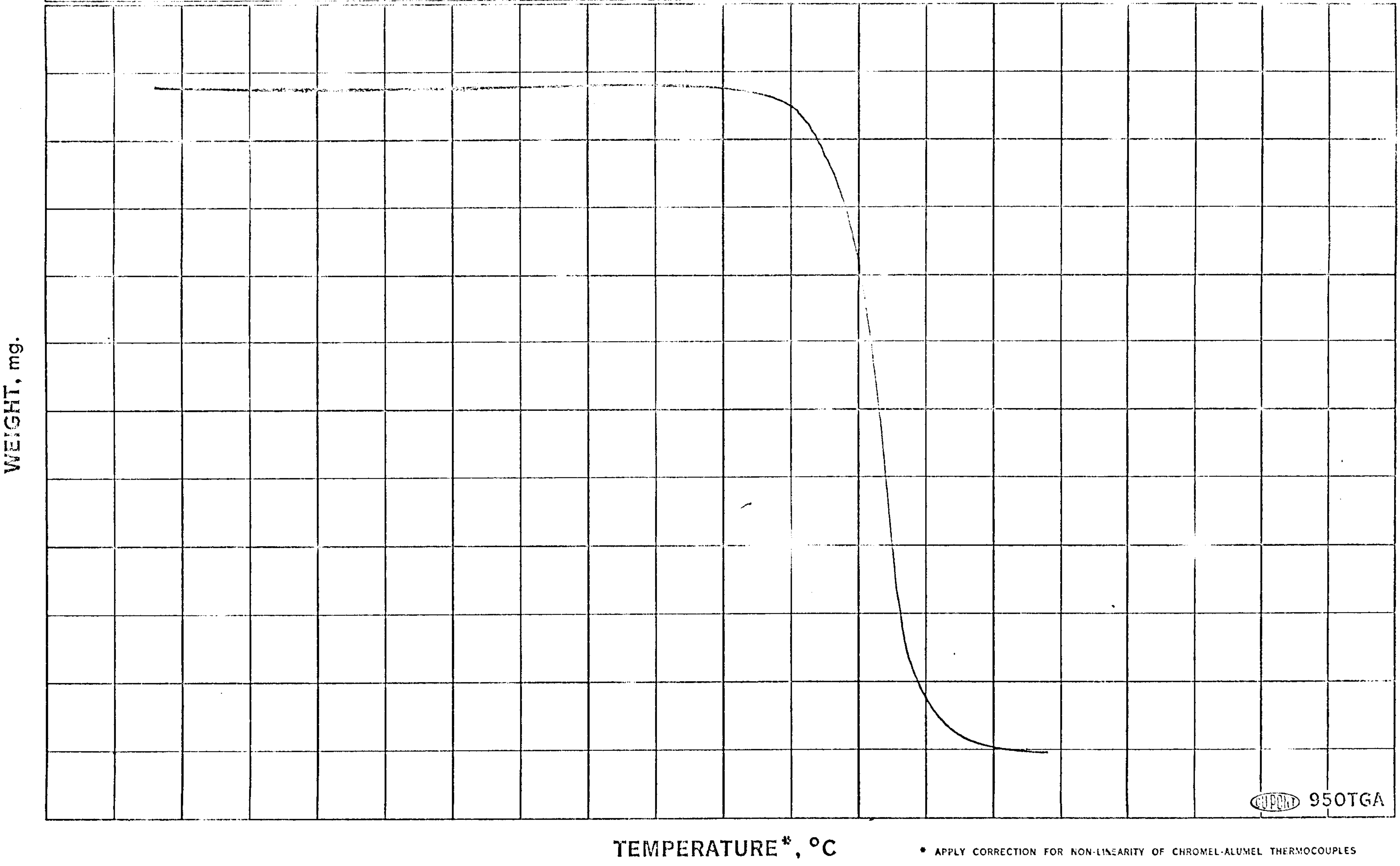
DATE 8-27-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. air

TIME CONSTANT 2 s.



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

Appendix No. 10

Appendix No. 11

DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-29-276

$\{N\text{-}\overset{m}{C_6H_4}\text{-}N{=}HC\text{-}C_6H_4\text{-}CH\}_n$

yellow polymer

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 7-9-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. nitrogen

TIME CONSTANT 2 sec.

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

Appendix No. 12

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-29-276

$\left[N-\overset{m}{C_6H_4}-N=HC-C_6H_4-CH\right]_n$

yellow polymer

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.

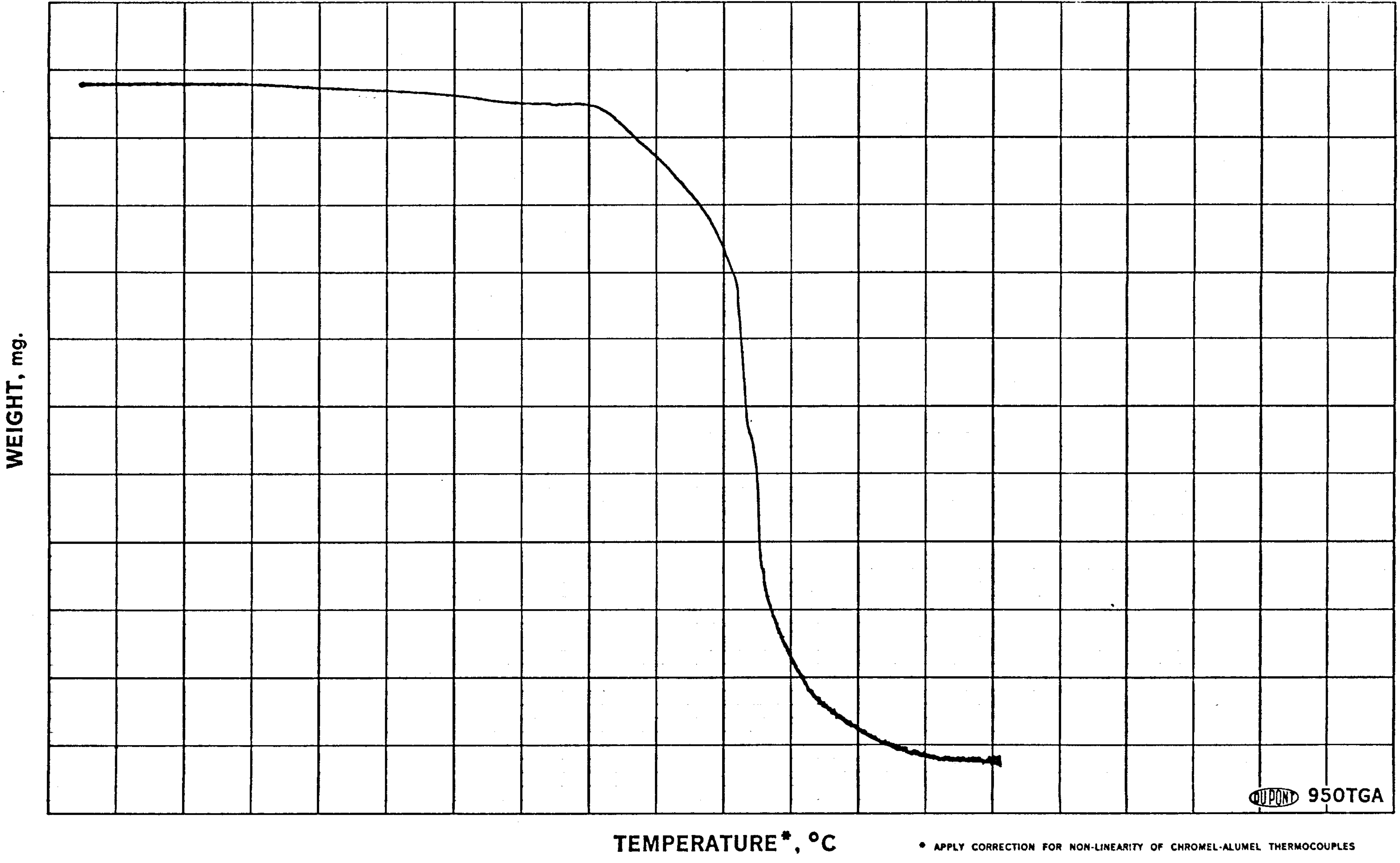
RUN NO. ____ DATE 7-2-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. air

TIME CONSTANT 2 sec.



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

DUPONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-29-284
$\{N-C_6H_4-C_6H_4-N=HC-C_6H_4-CH\}_n$
SIZE 10 mg.

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

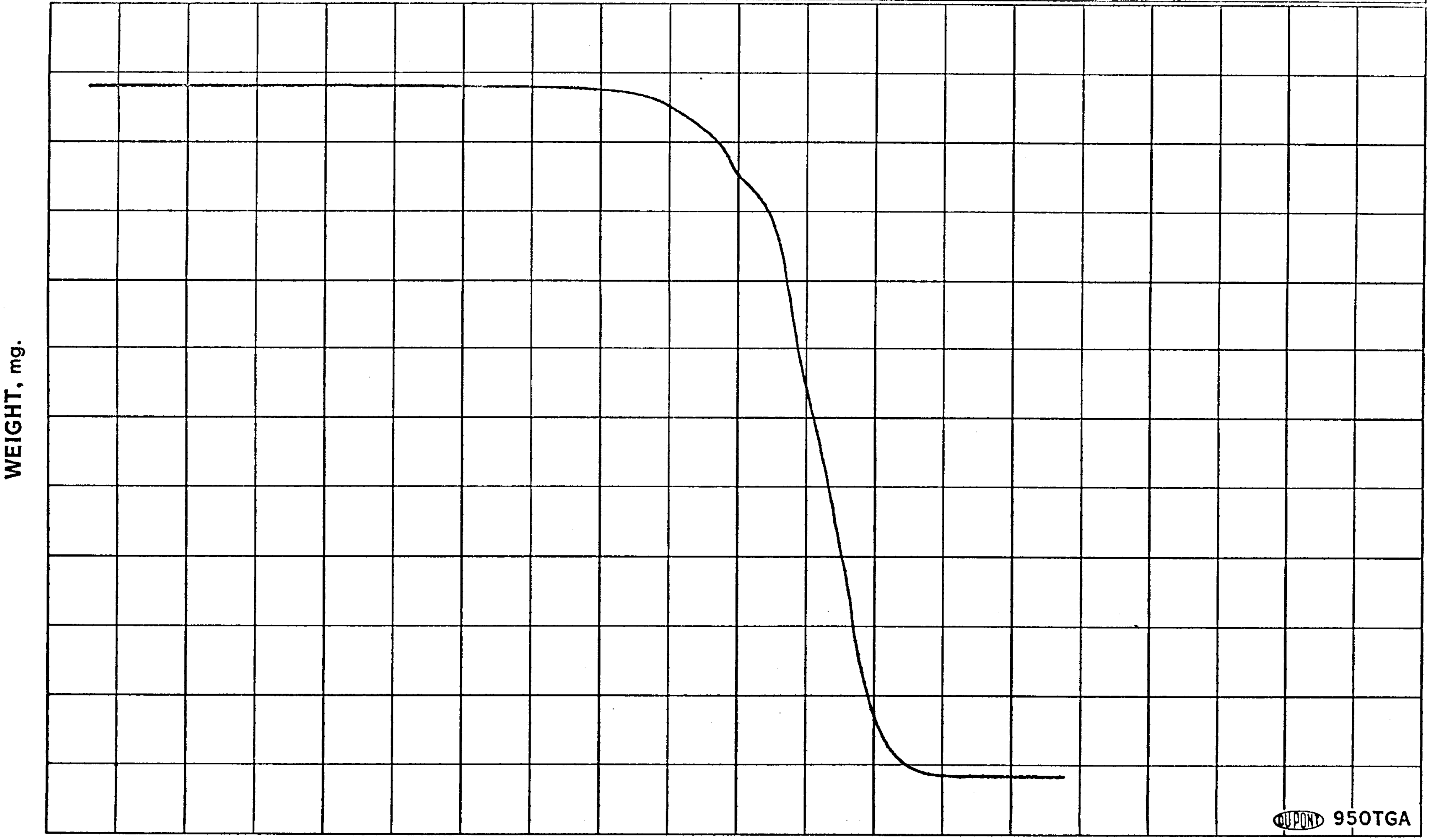
Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. ______ DATE 7-16-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. nitrogen
TIME CONSTANT 2 sec.

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

INSTRUMENT PRODUCTS DIVISION

SAMPLE: DA-29-284	X-AXIS	Y-AXIS	RUN NO. ______ DATE 7-21-65
$\left[N-C_6H_4-C_6H_4-N=HC-C_6H_4-CH\right]_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR JVC
	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

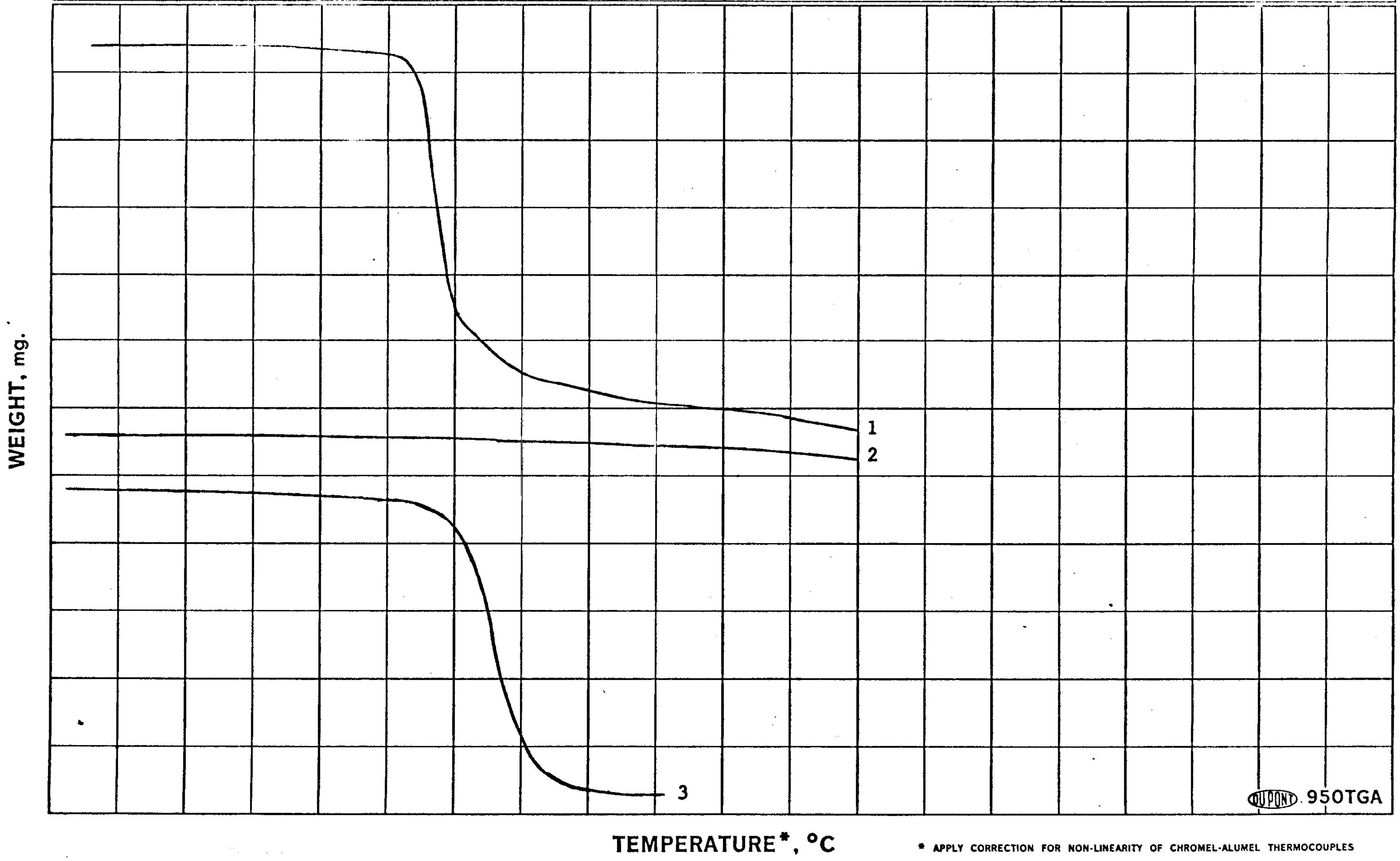
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 14

Appendix No. 15

DUPONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-29-284	**X-AXIS**	**Y-AXIS**	RUN NO. ____ DATE 8-28-65
$\{N-C_6H_4-C_6H_4-N=HC-C_6H_4-CH\}_n$	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR JVC
	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. (1) N_2, (2) 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

Appendix No. 16

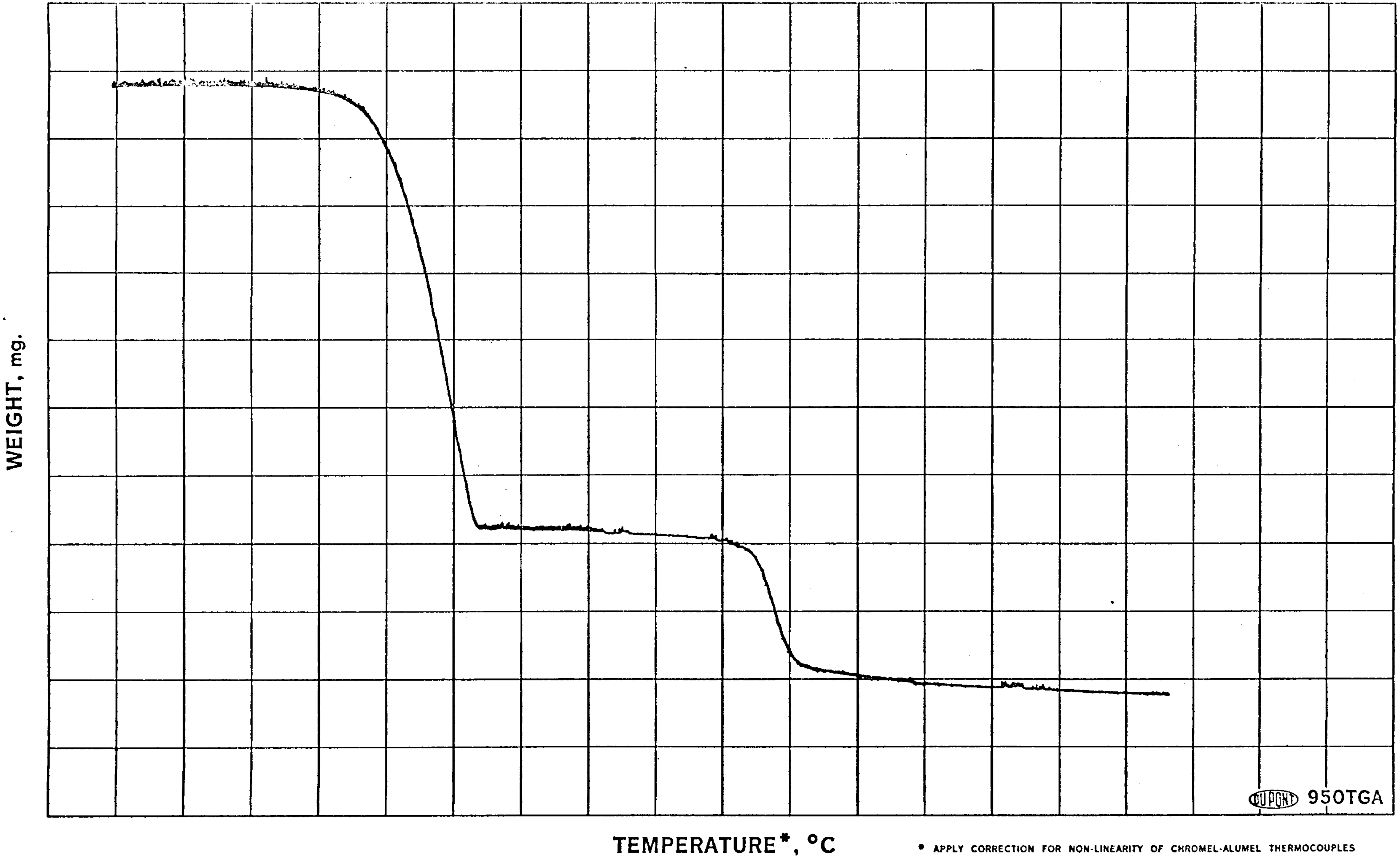
DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-29-277
$\{N-C_6H_4-C_6H_4-N=HC-C_6H_4-CH\}_n$
yellow polymer
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 7-11-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. nitrogen
TIME CONSTANT 2 sec.



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

SAMPLE: DA-29-277

$[N{-}C_6H_4{-}C_6H_4{-}N{=}HC{-}C_6H_4{-}CH{=}]_n$

yellow polymer

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.

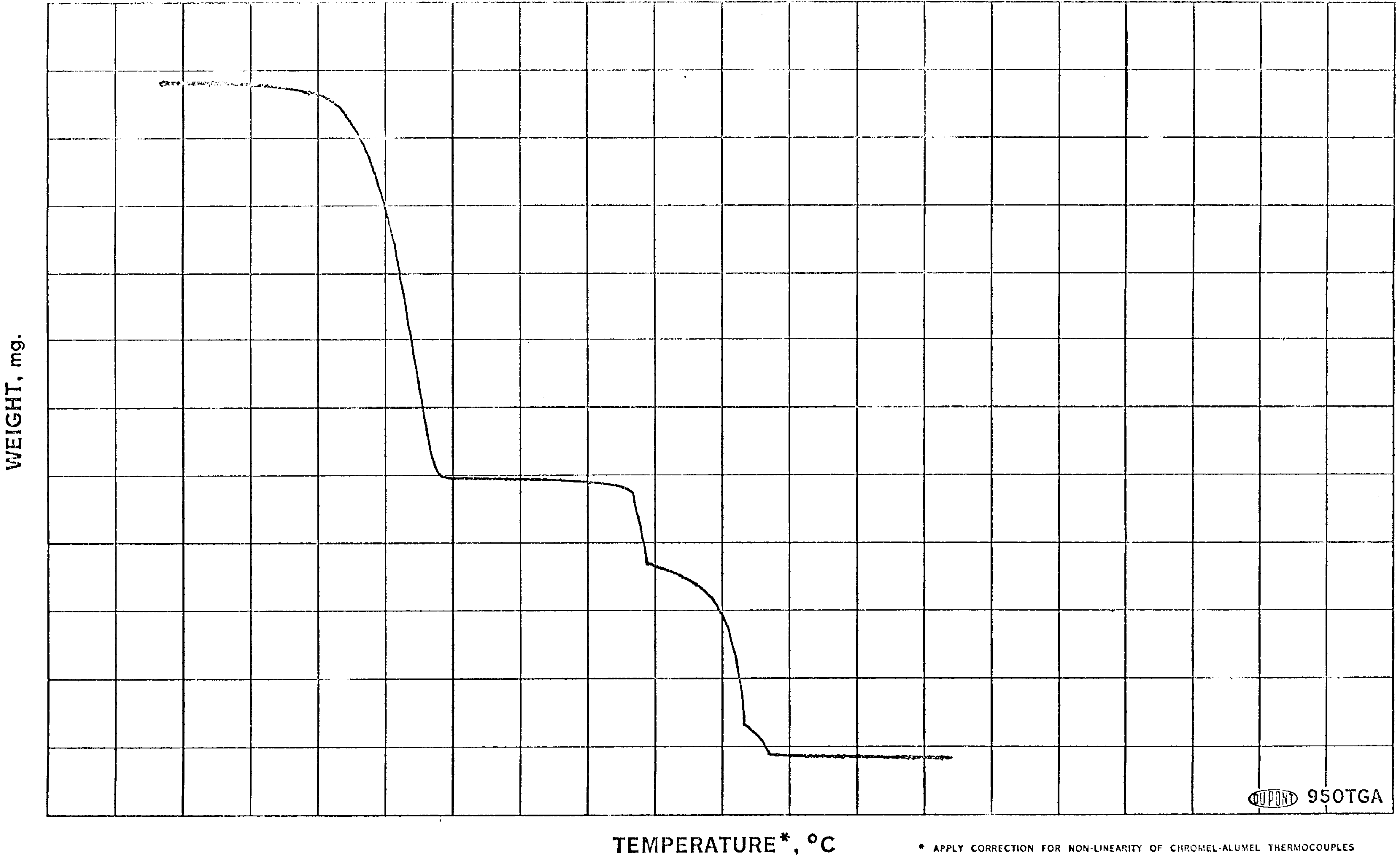
RUN NO. DATE 7-22-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. air

TIME CONSTANT 2 sec.



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

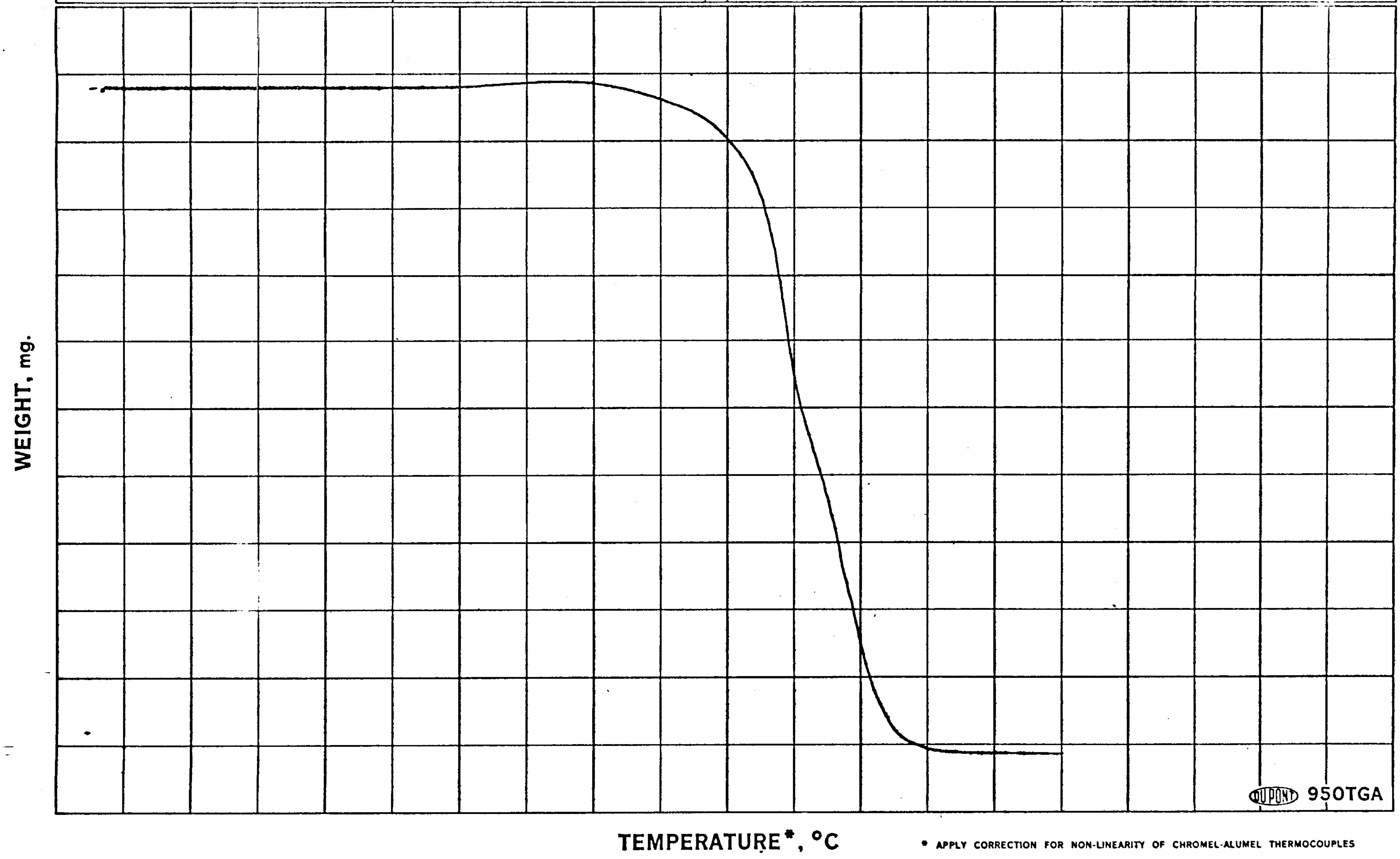
E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-29-265	X-AXIS	Y-AXIS	RUN NO. ____ DATE 7-16-65
$\{N-C_6H_4-CH_2-C_6H_4-N=HC-C_6H_4-CH\}_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR JVC
	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. nitrogen
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.

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

INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-29-265	X-AXIS	Y-AXIS	RUN NO.____ DATE 7-21-65
$\{N-C_6H_4-CH_2-C_6H_4-N=HC-C_6H_4-CH=\}_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR JVC
	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. air
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



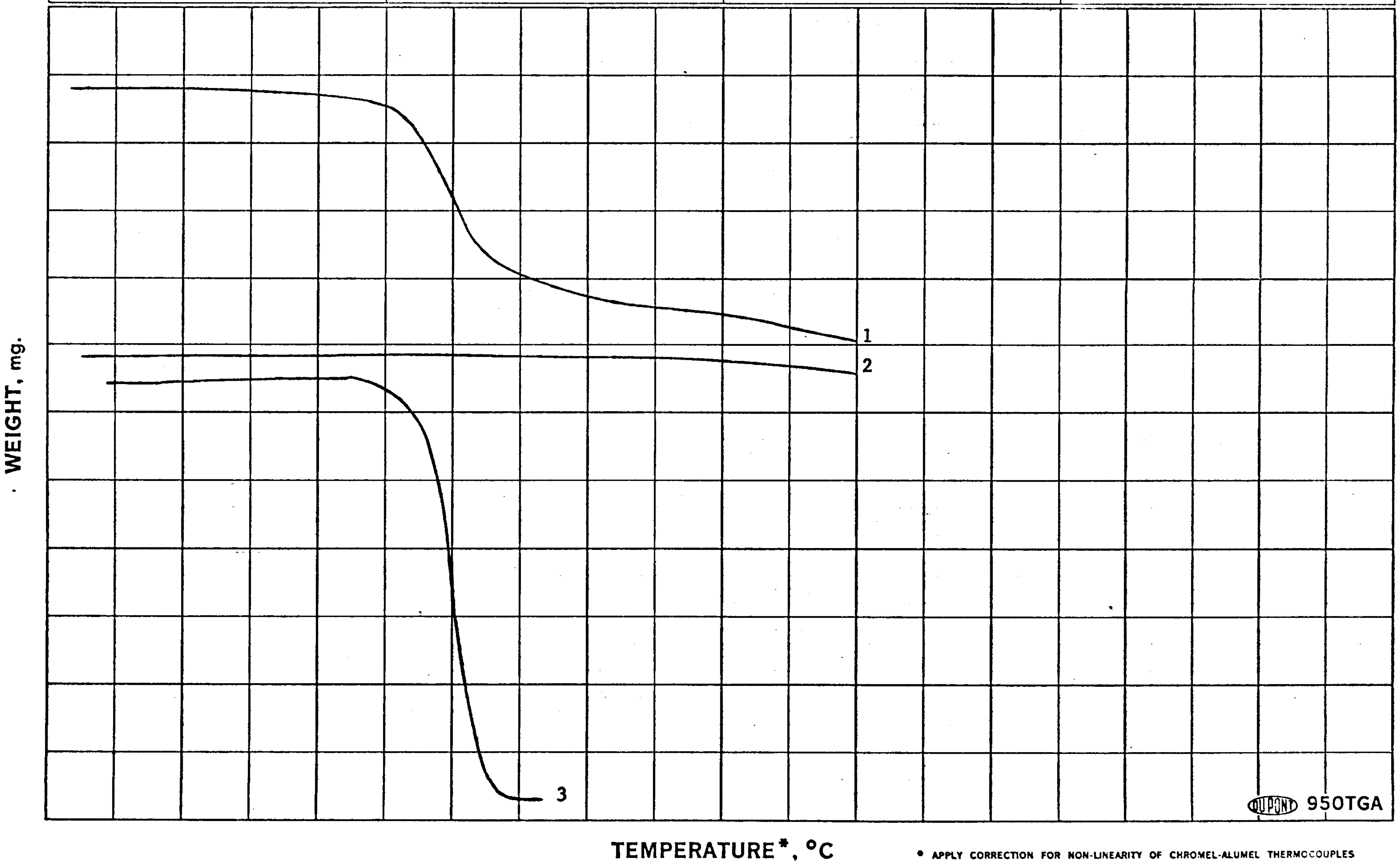
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 19

Appendix No. 20

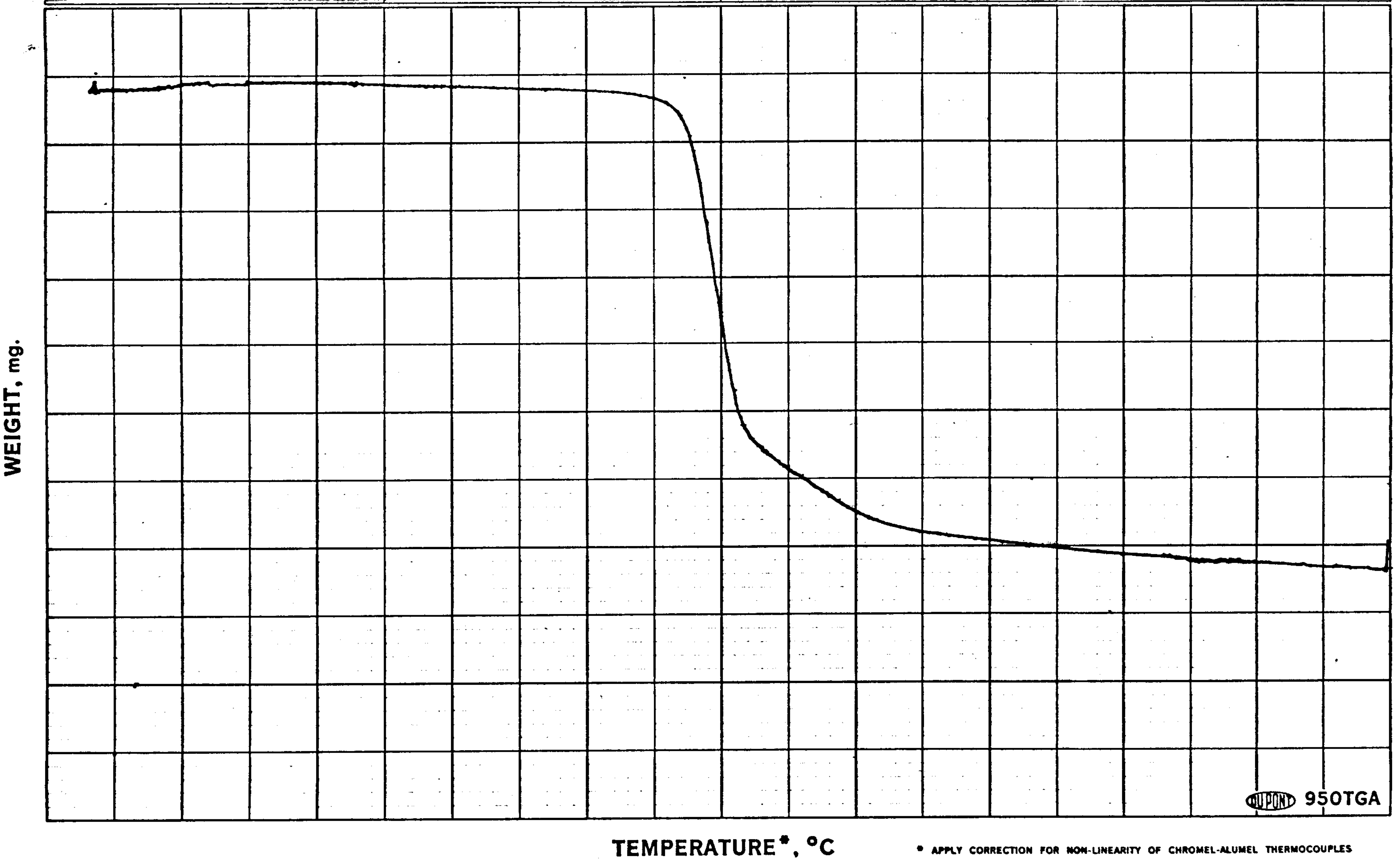
DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-29-265	X-AXIS	Y-AXIS	RUN NO. ____ DATE 8-26-65
$\left[N-C_6H_4-CH_2-C_6H_4-N=HC-C_6H_4-CH\right]_n$	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR JVC HEATING RATE 15 °C/min.
	SHIFT 0 inch		ATM. (1) N_2, (2) 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

SAMPLE: DA-29-266	X-AXIS	Y-AXIS	RUN NO._____ DATE 9-11-65
$\mp[N-C_6H_4-CH_2-C_6H_4-N=HC-C_6H_4-CH\mp]_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch	OPERATOR JVC
yellow polymer	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C/min.
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	ATM. nitrogen
			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-29-266
$[N-C_6H_4-CH_2-C_6H_4-N=HC-C_6H_4-CH]_n$
yellow Polymer
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 JVC
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-29-275

$[N-C_6H_4-O-C_6H_4-N{=}HC-C_6H_4-CH]_n$

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.

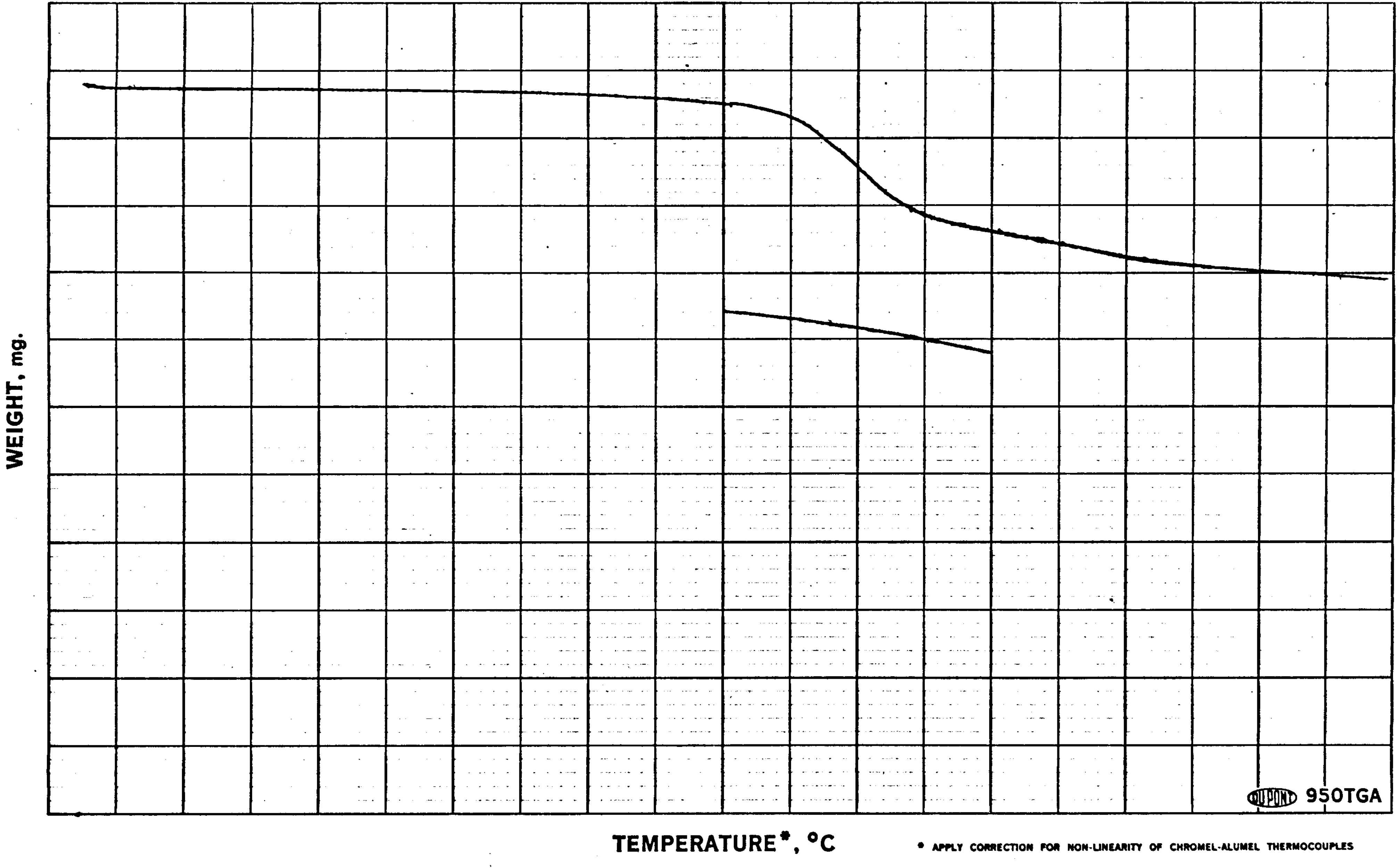
RUN NO. ____ DATE 7-15-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. nitrogen

TIME CONSTANT 2 sec.



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

Appendix No. 23

Appendix No. 24

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

SAMPLE: DA-29-275

$\ddagger N-C_6H_4-O-C_6H_4-N{=}HC-C_6H_4-CH\ddagger_n$

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.

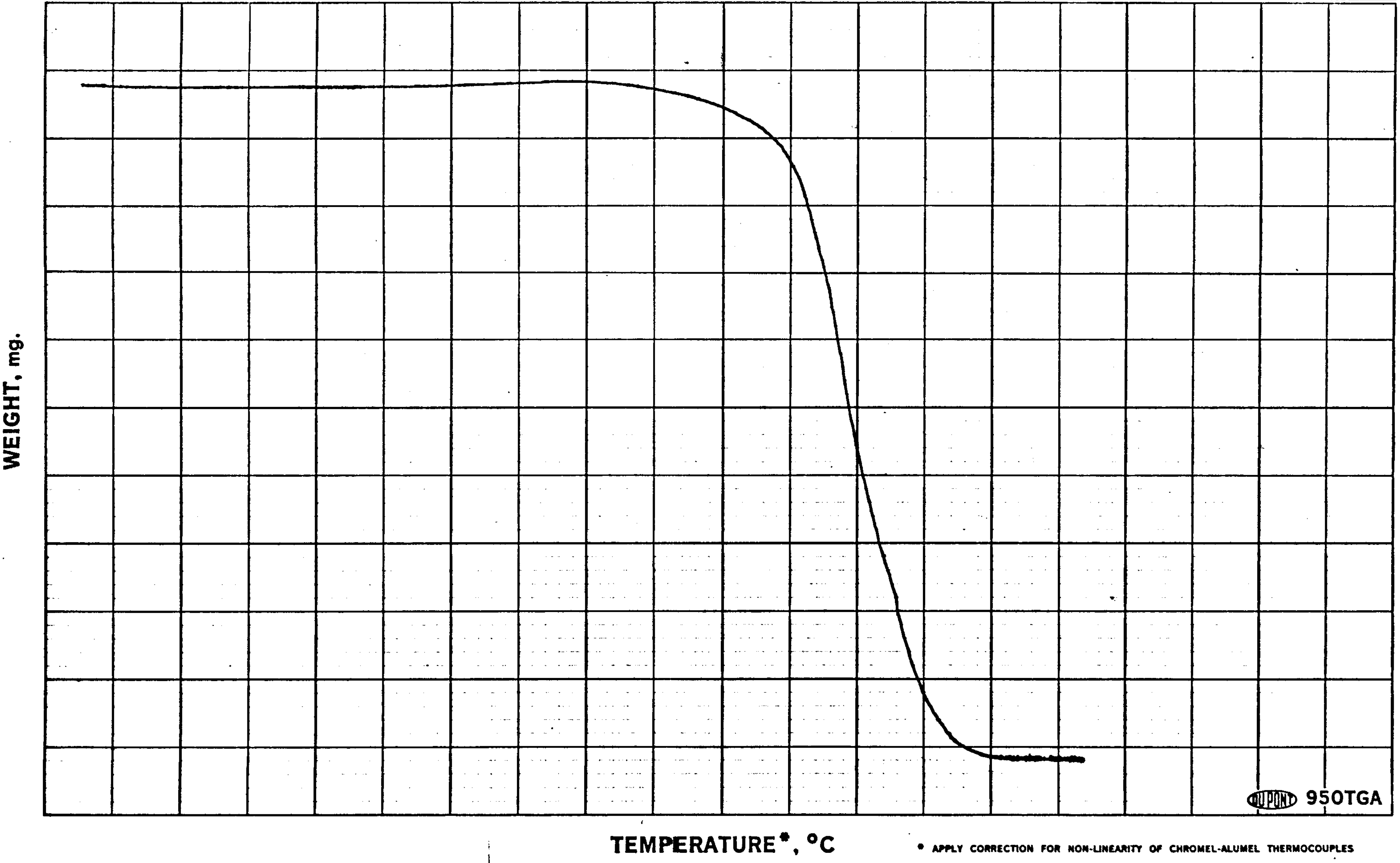
RUN NO. DATE 7-16-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. air

TIME CONSTANT 2 sec.



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

Appendix No. 25

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

SAMPLE: DA-29-275

$\{N-C_6H_4-O-C_6H_4-N{=}HC-C_6H_4-CH\}_n$

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.

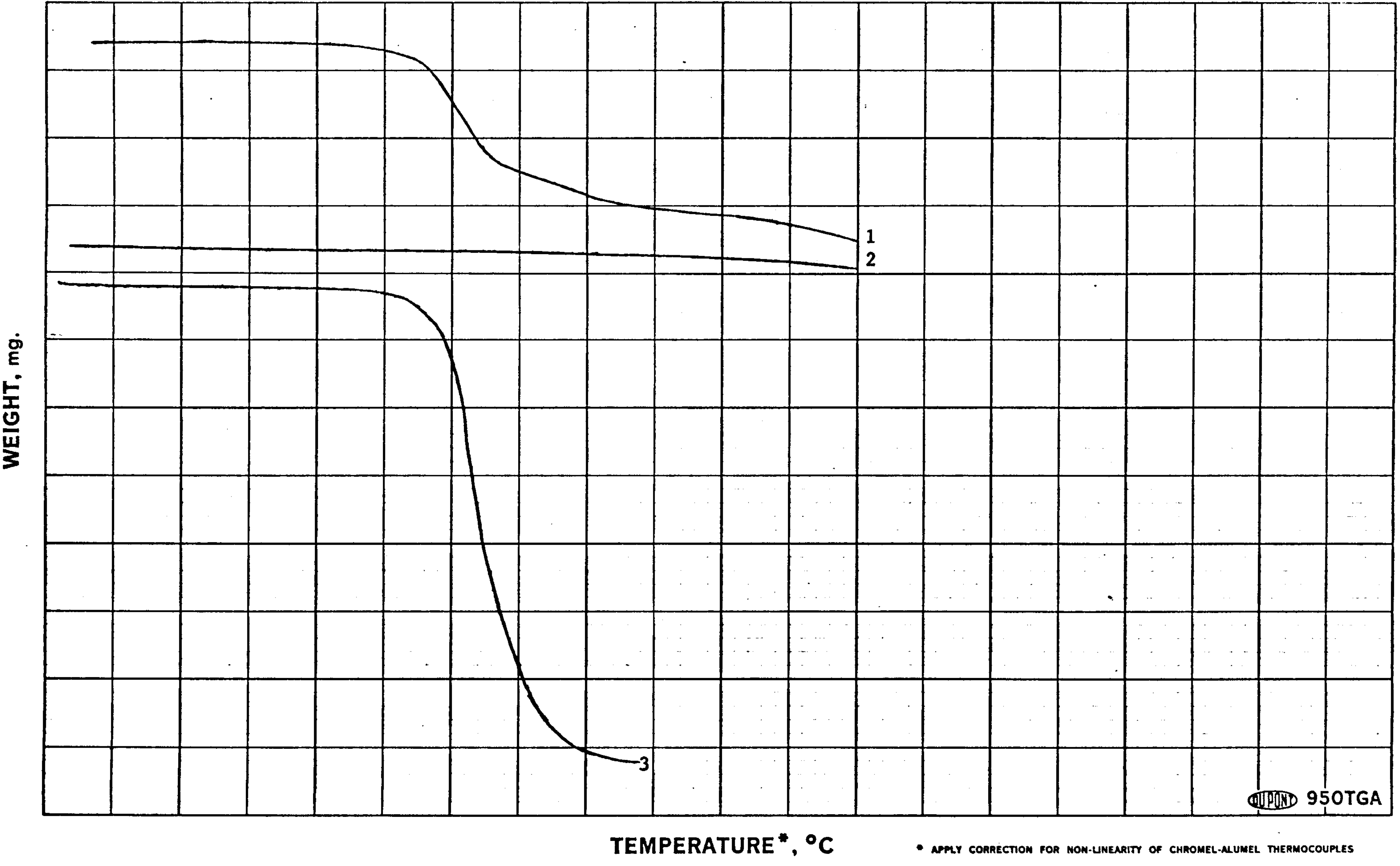
DATE 9-13-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. (1) N_2, (2) N_2, (3) air

TIME CONSTANT 2 sec.



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

Appendix No. 26

DUPONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-29-271	X-AXIS	Y-AXIS	RUN NO. ___ DATE 9-13-65
$\{N-C_6H_4-O-C_6H_4-N=HC-C_6H_4-CH\}_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch	OPERATOR JVC
yellow polymer	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C/min.
			ATM. nitrogen
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.

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

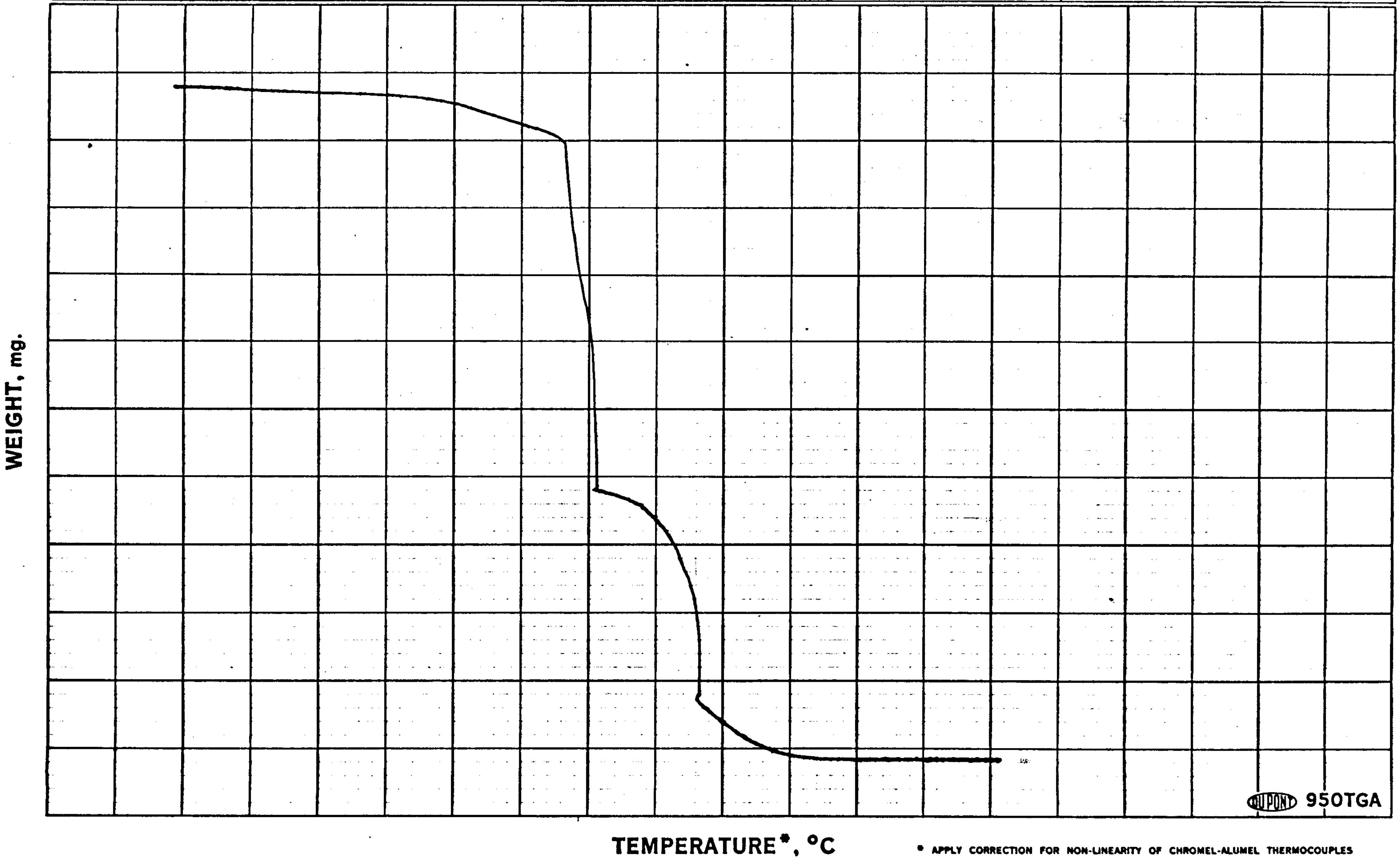
DU PONT | E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-29-271
$\{N-C_6H_4-O-C_6H_4-N{=}HC-C_6H_4-CH\}_n$
yellow polymer
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 JVC
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



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

Appendix No. 28

DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-29-282

$\{N-C_6H_4-NH-C_6H_4-N=HC-C_6H_4-CH\}_n$

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.

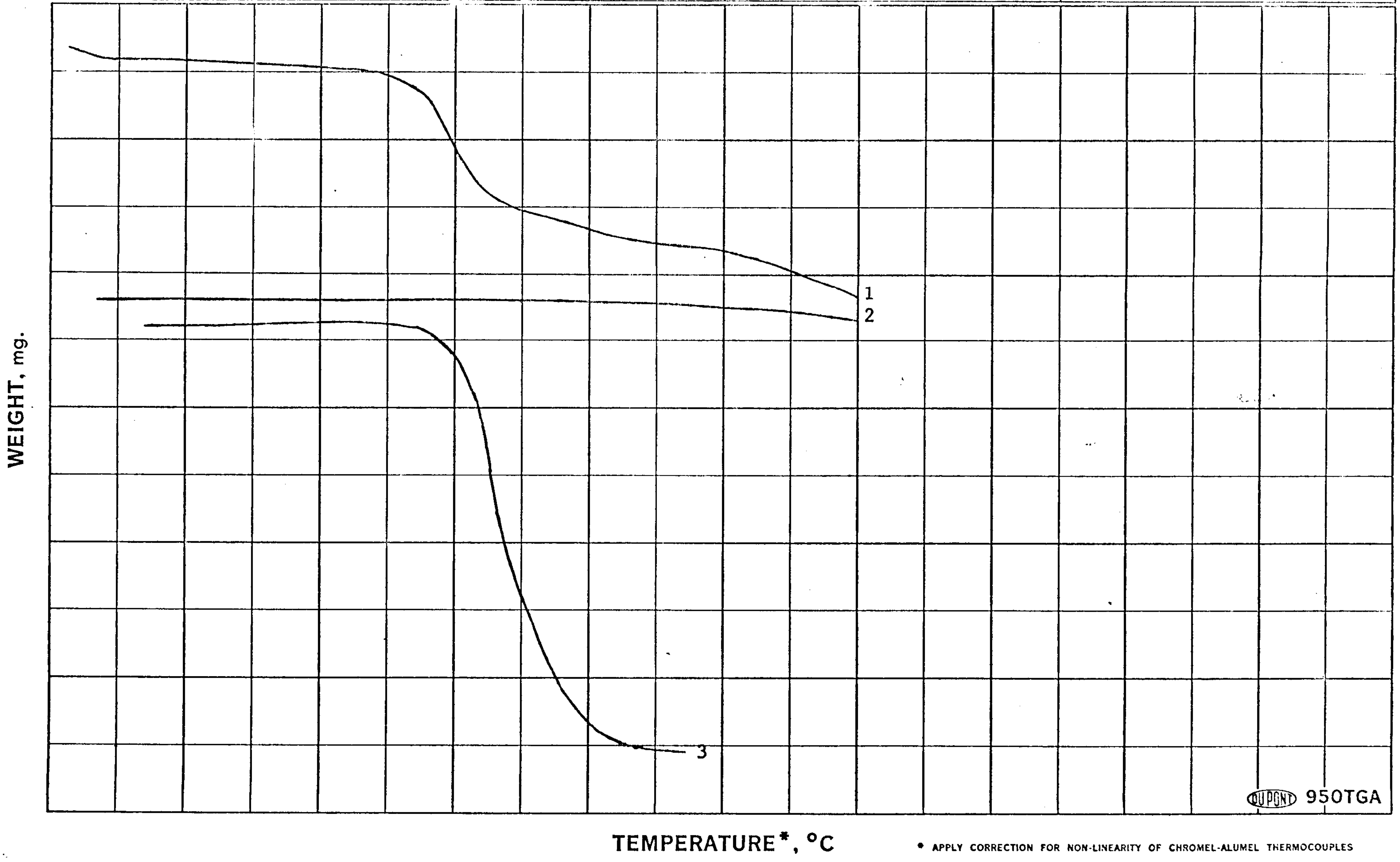
RUN NO. ______ DATE 9-13-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM.(1) N_2, (2) N_2, (3) air

TIME CONSTANT 2 sec.



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

Appendix No. 29

SAMPLE: DA-29-282

$\{N-C_6H_4-NH-C_6H_4-N=HC-C_6H_4-CH\}_n$

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.

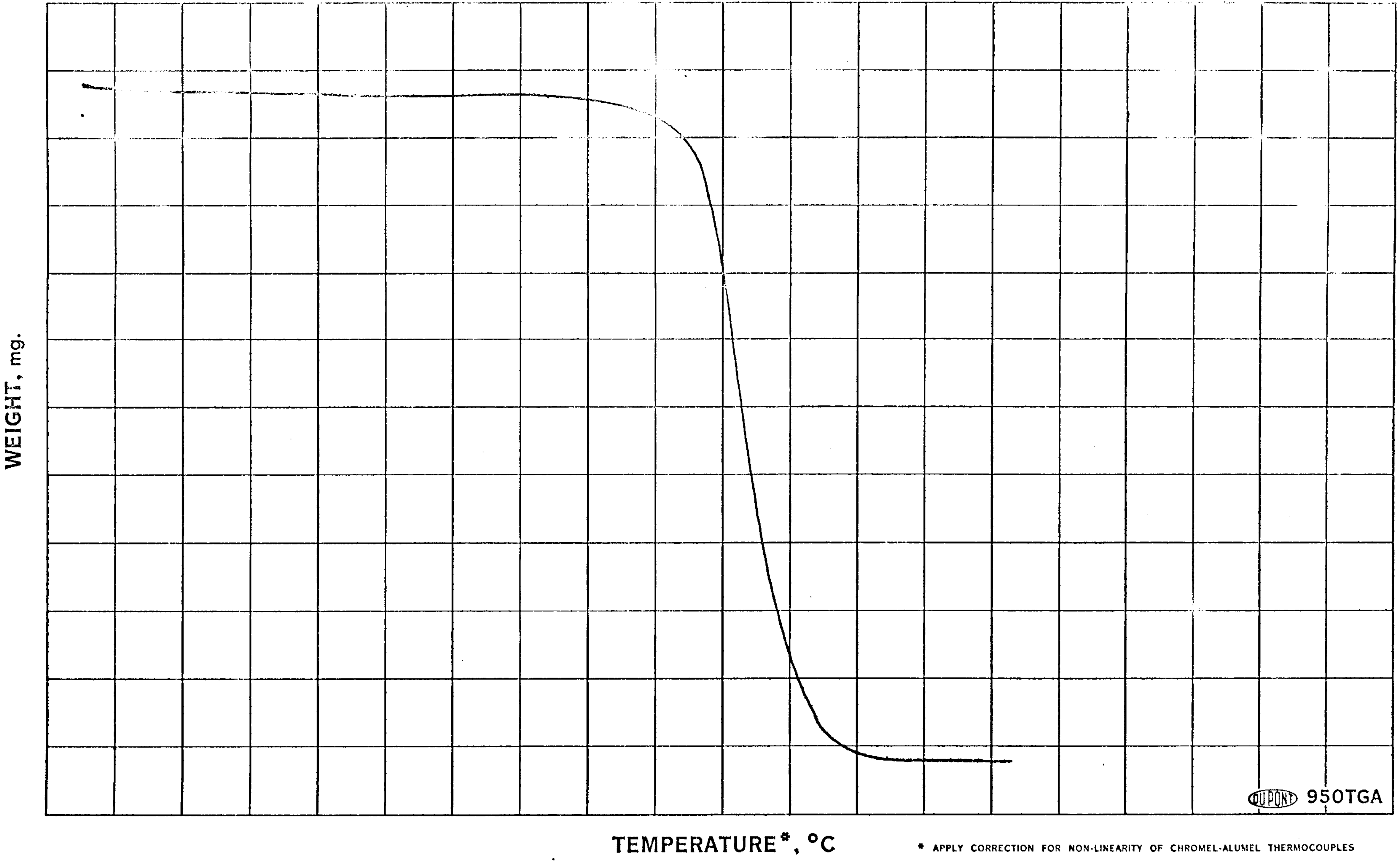
DATE 7-21-

OPERATOR JVC

HEAT RATE 15 °C/min.

ATM. air

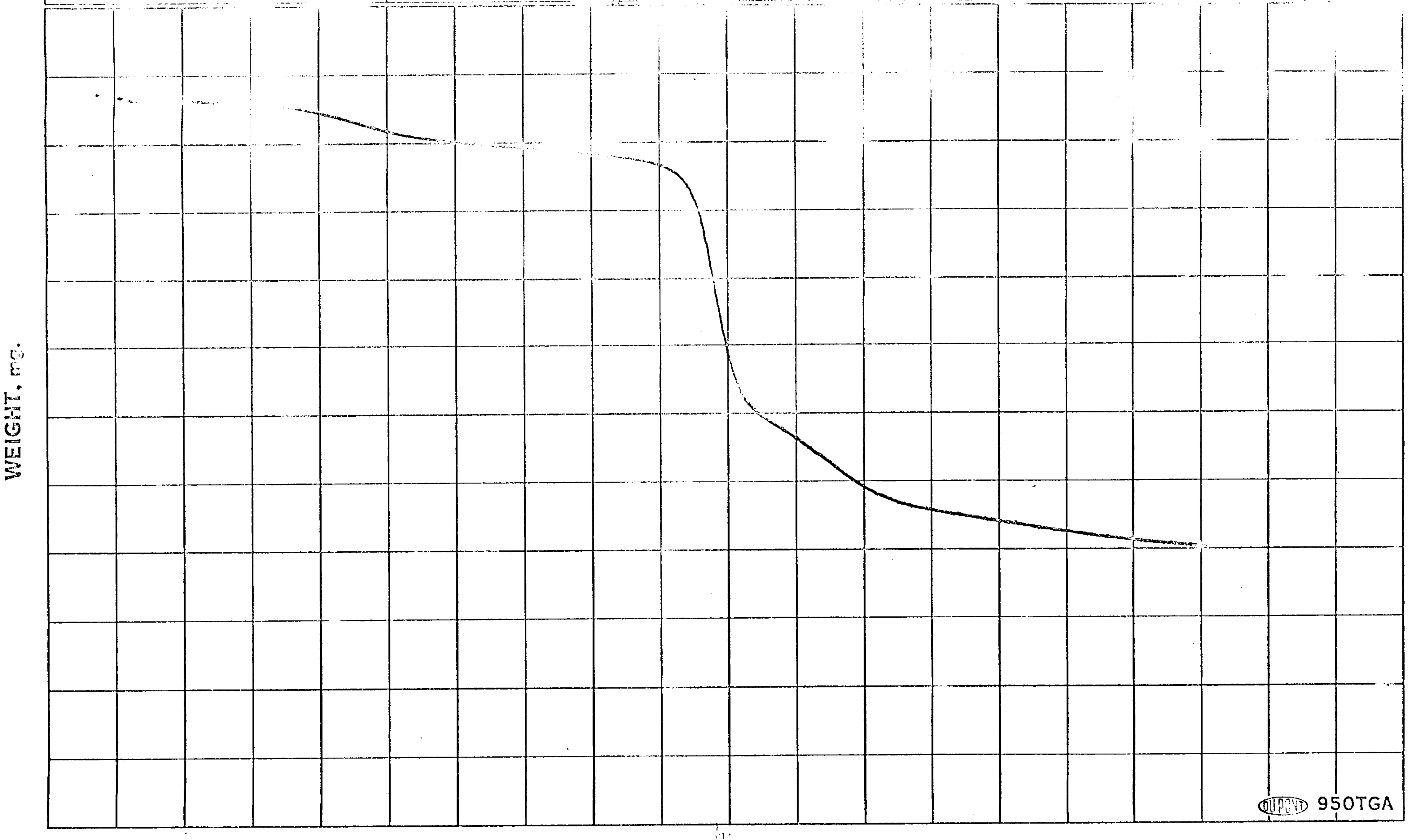
TIME CONSTA 2 sec.



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

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-29-281	X-AXIS	Y-AXIS	RUN NO. ____ DATE 7-13-65
$\{N-C_6H_4-NH-C_6H_4-N=HC-C_6H_4-CH\}_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR JVC
orange polymer	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. Nitrogen
SIZE 10 mg.	TIME SCALE (ALT.)	SUPPRESSION 0 mg.	TIME CONST. 2 sec.

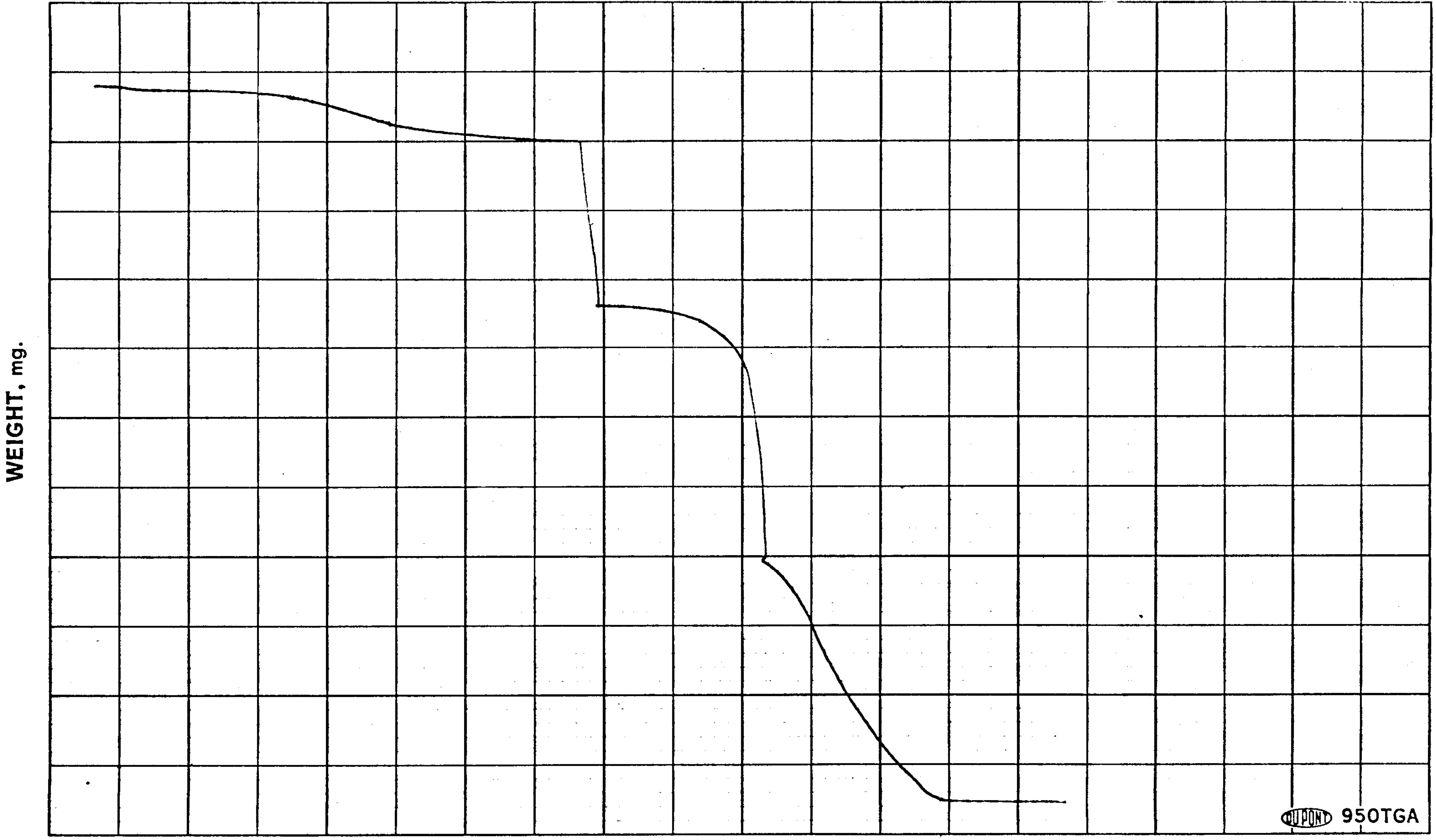


TEMPERATURE*, °C

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

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

SAMPLE: DA-29-281 $\{N-C_6H_4-NH-C_6H_4-N=HC-C_6H_4-CH\}_n$ orange polymer 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 JVC HEATING RATE 15 °C/min. ATM. air TIME CONSTANT 2 sec.



TEMPERATURE*, °C

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

Appendix No. 32

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

SAMPLE: DA-42-16

$\{N-C_6H_4-S-C_6H_4-N=HC-C_6H_4-CH\}_n$

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.

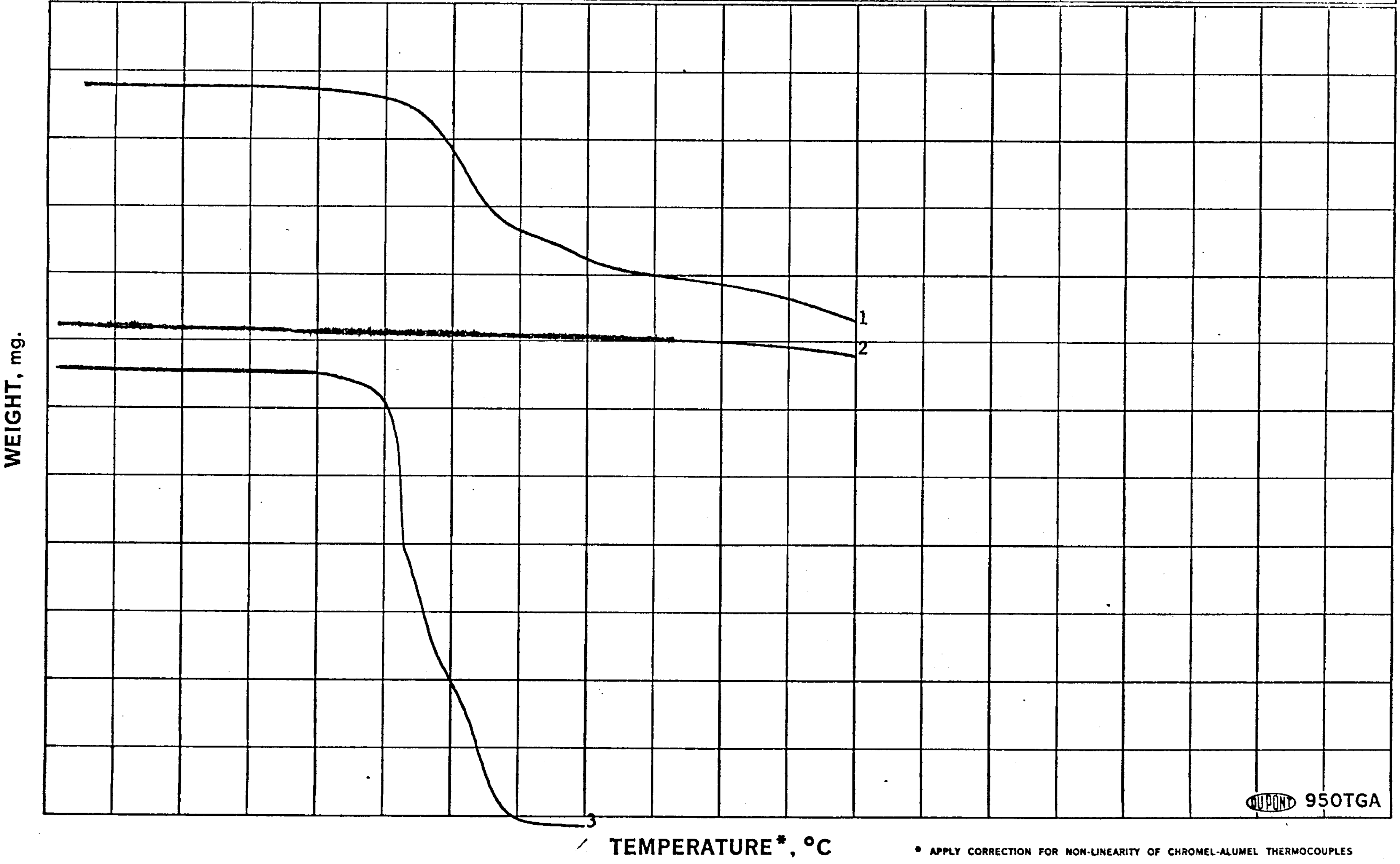
RUN NO. DATE 9-12-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. (1) N_2, (2) N_2, (3) air

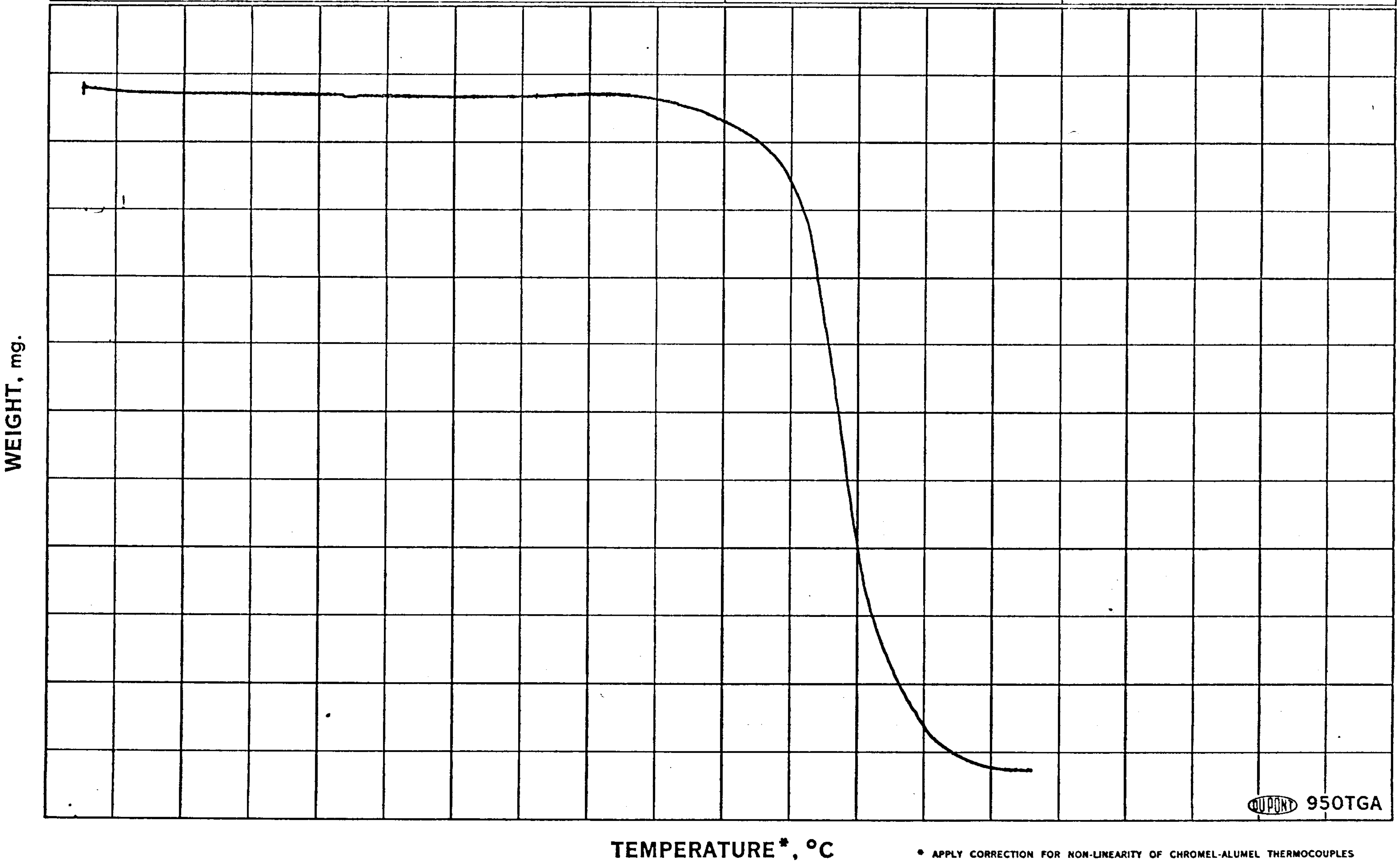
TIME CONSTANT 2 sec.



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

INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-42-16 $\{N-C_6H_4-S-C_6H_4-N{=}HC-C_6H_4-CH\}_n$ 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 9-12-65 OPERATOR JVC HEATING RATE 15 °C/min. ATM. air TIME CONSTANT 2 sec.



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

Appendix No. 33

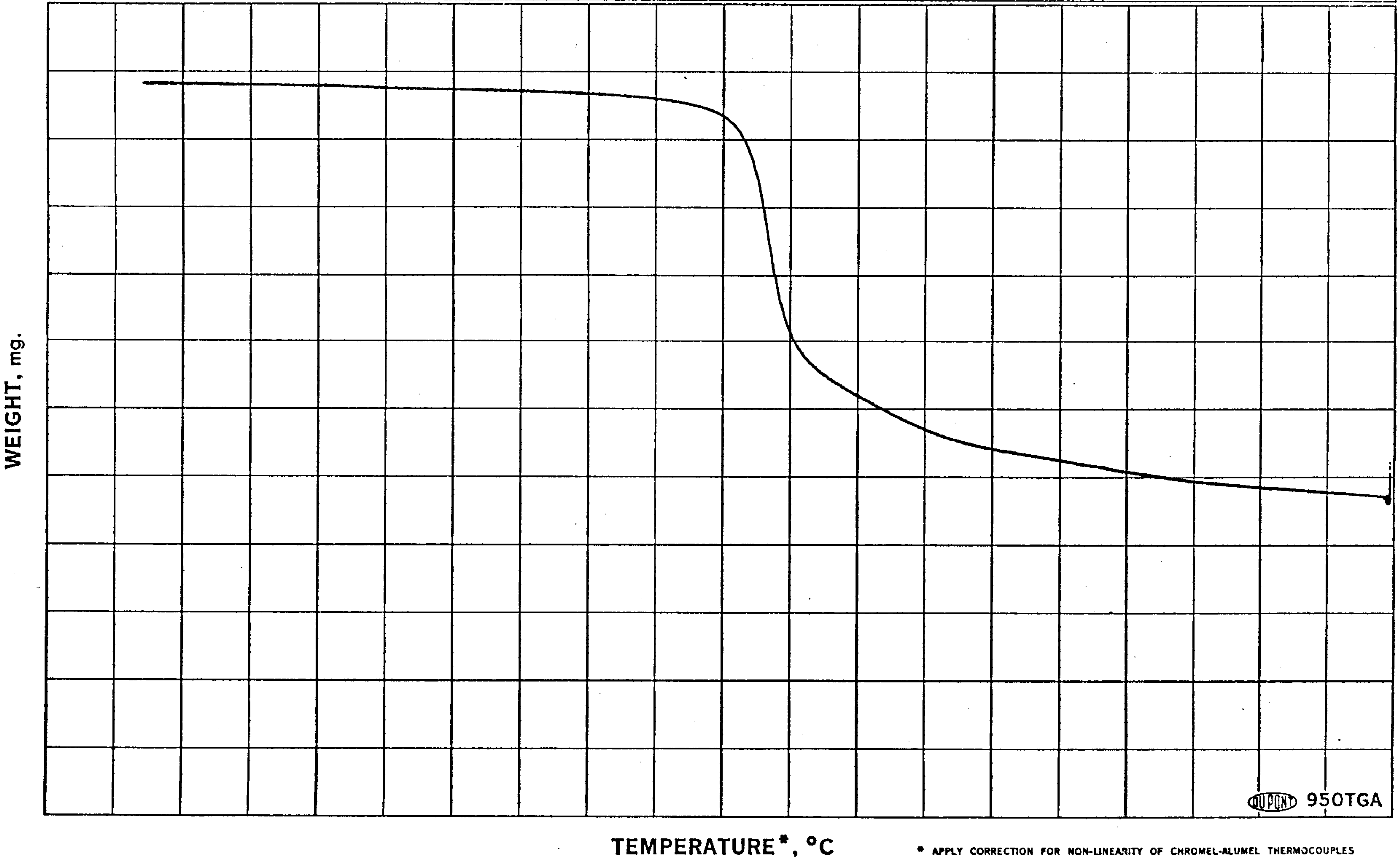
DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-42-15
$\{N-C_6H_4-S-C_6H_4-N{=}HC-C_6H_4-CH\}_n$
yellow polymer
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 9-14-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. nitrogen
TIME CONSTANT 2 sec.

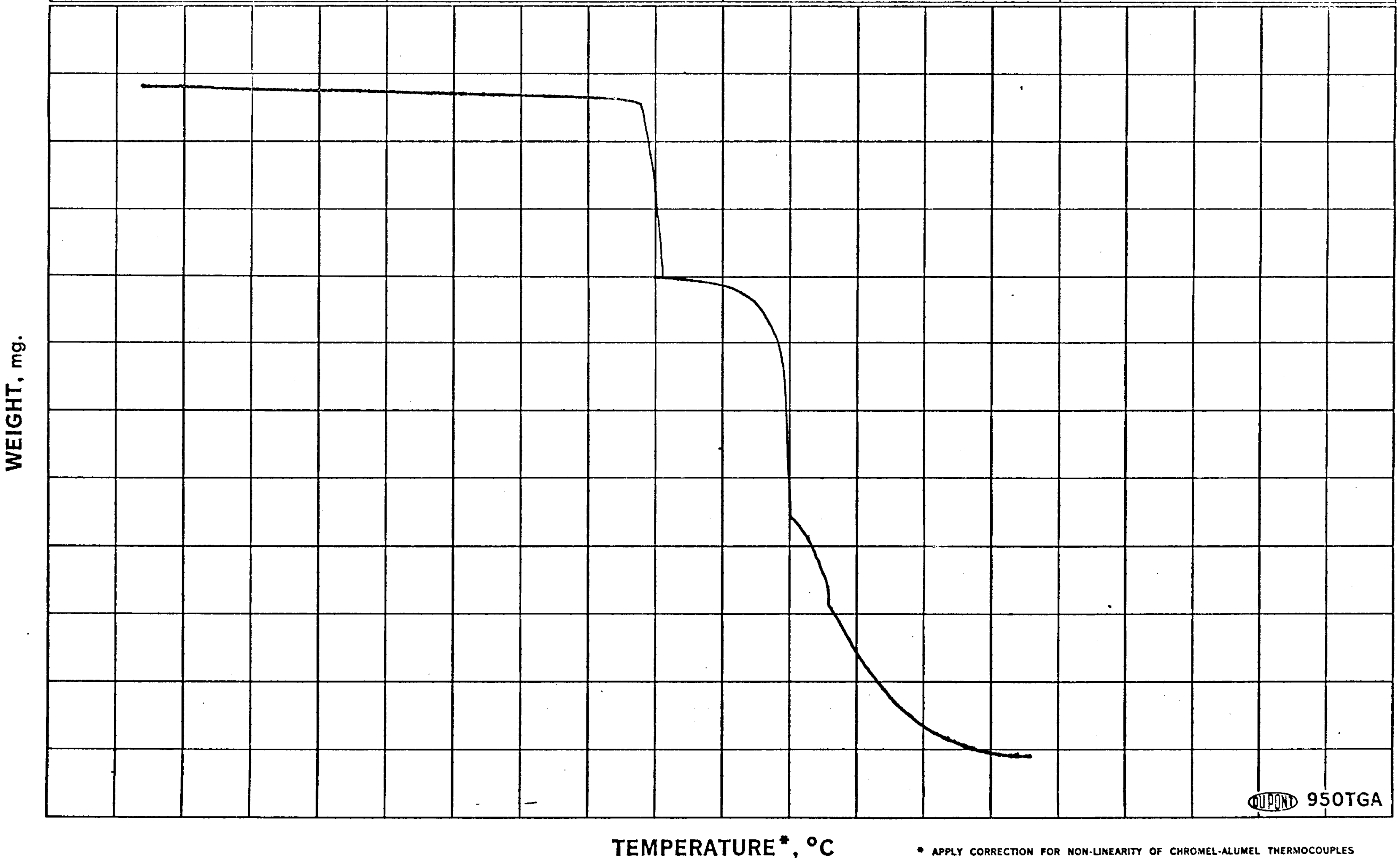


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 34

DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-42-15	X-AXIS	Y-AXIS	RUN NO. ____ DATE 9-14-65
$\text{+}N\text{-}C_6H_4\text{-}S\text{-}C_6H_4\text{-}N\text{=}HC\text{-}C_6H_4\text{-}CH\text{+}_n$ yellow polymer	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR JVC
	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. air
SIZE 9.5 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



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

Appendix No. 35

Appendix No. 36

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-29-285
$\{N-C_6H_4-SO_2-C_6H_4-N{=}HC-C_6H_4-CH{=}\}_n$
SIZE 9.8 mg.

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

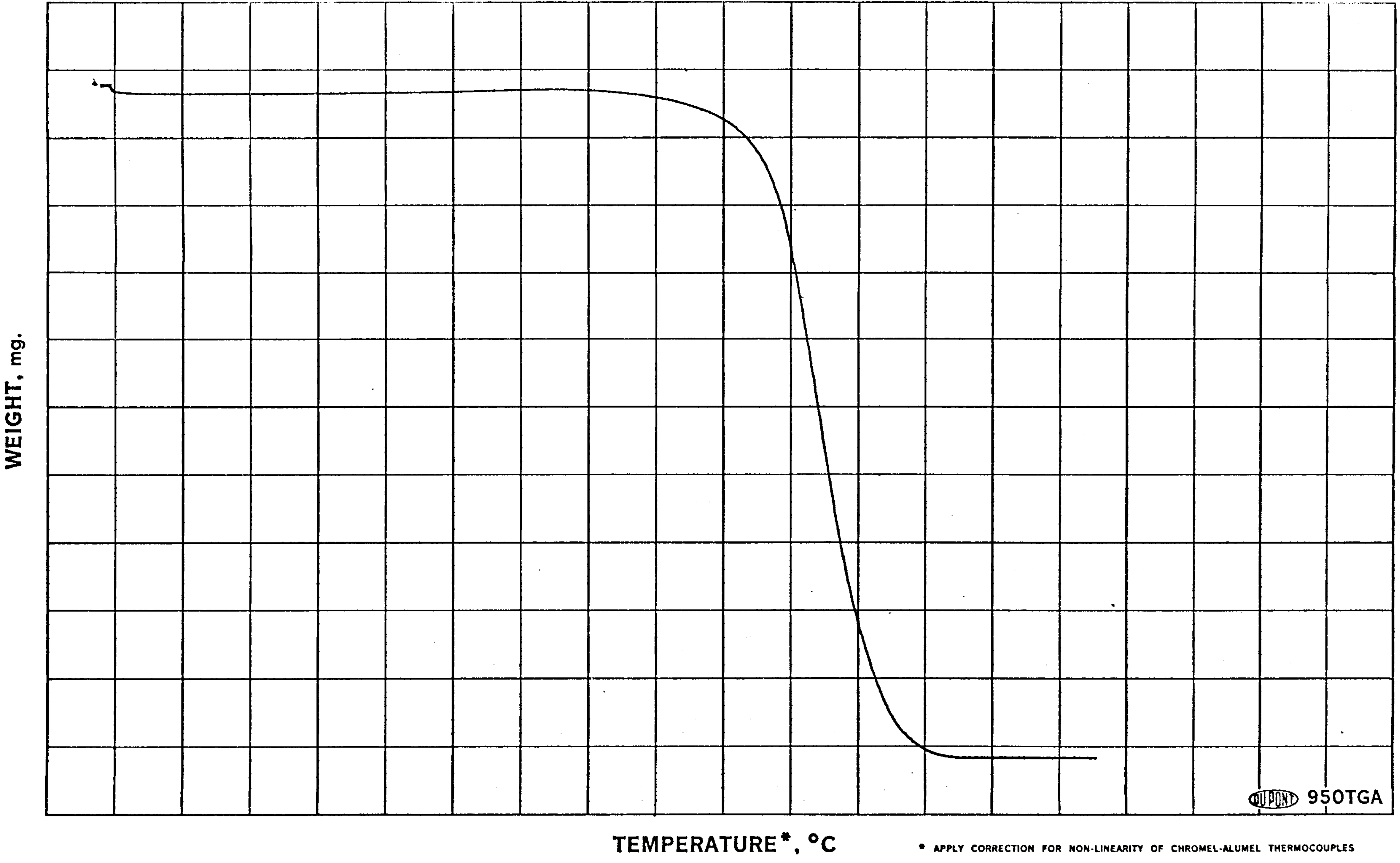
Y-AXIS
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

RUN NO. DATE 7-19-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. nitrogen
TIME CONSTANT 2 sec.

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

DUPONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-29-285	X-AXIS	Y-AXIS	RUN NO. ______ DATE 7-20-65
$[N-C_6H_4-SO_2-C_6H_4-N=HC-C_6H_4-CH=]_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR JVC
	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-29-285

$\{N-C_6H_4-SO_2-C_6H_4N=HC-C_6H_4-CH\}_n$

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.

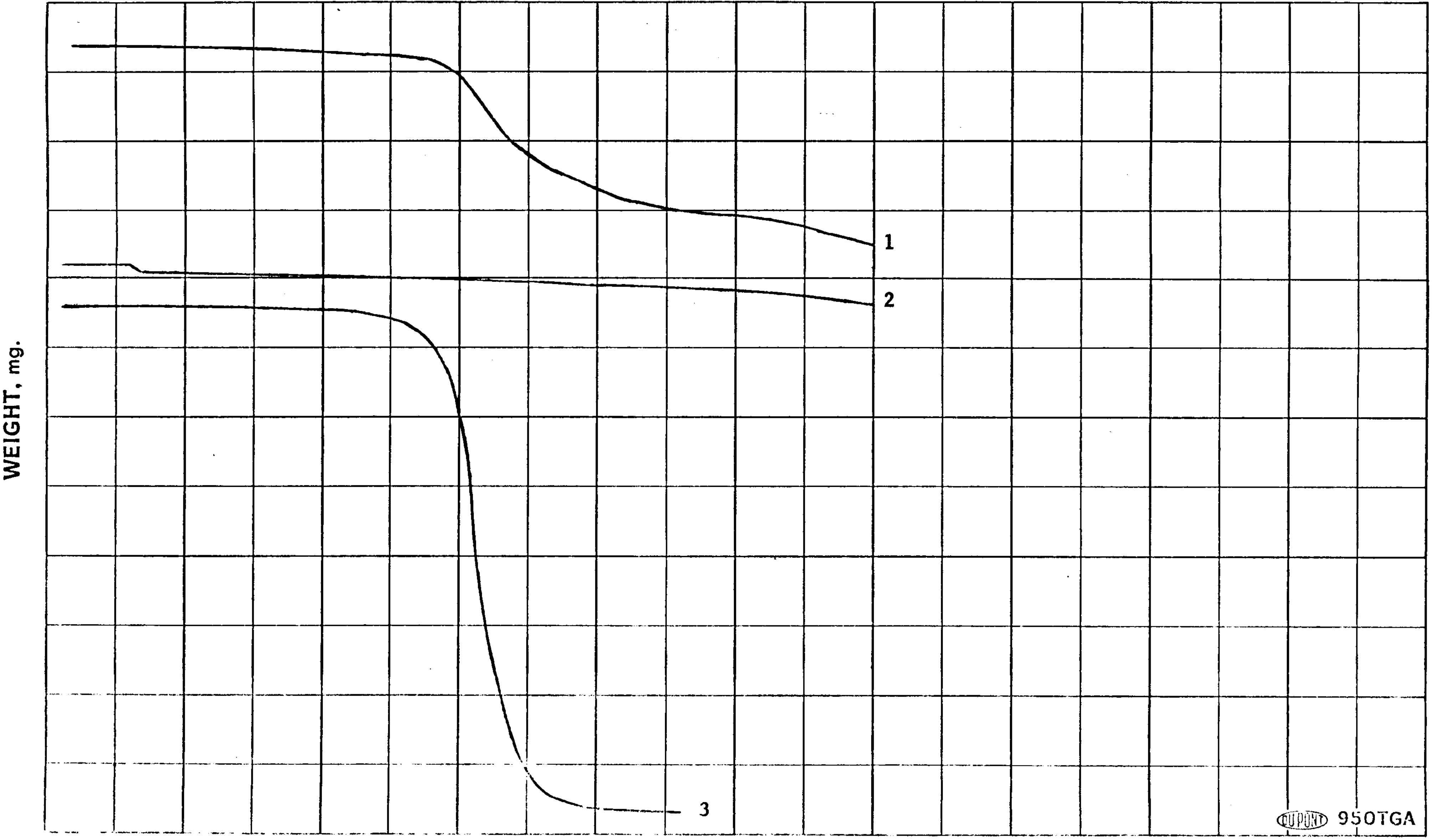
RUN NO. ____ DATE 8-24-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. (1) N_2, (2) N_2, (3) air

TIME CONSTANT 2 sec.



TEMPERATURE*, °C

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

Appendix No. 39

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

	X-AXIS	Y-AXIS	
SAMPLE: DA-29-270	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch	RUN NO. ____ DATE 7-10-65
$\{N-C_6H_4-SO_2-C_6H_4-N{=}HC-C_6H_4-CH{=}\}_n$	SHIFT 0 inch	(SCALE SETTING X 2)	OPERATOR JVC
yellow polymer	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	HEATING RATE 15 °C/min.
SIZE 10 mg.			ATM. nitrogen
			TIME CONSTANT 2 sec.

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

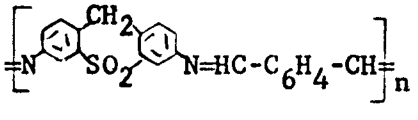
DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-29-270	X-AXIS	Y-AXIS	RUN NO. ___ DATE 7-22-65
$[N-C_6H_4-SO_2-C_6H_4-N{=}HC-C_6H_4-CH]_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch	OPERATOR JVC
yellow polymer	SHIFT 0 inch	(SCALE SETTING X 2)	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

DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON DELAWARE

SAMPLE: DA-42-11



SIZE 10 mg.

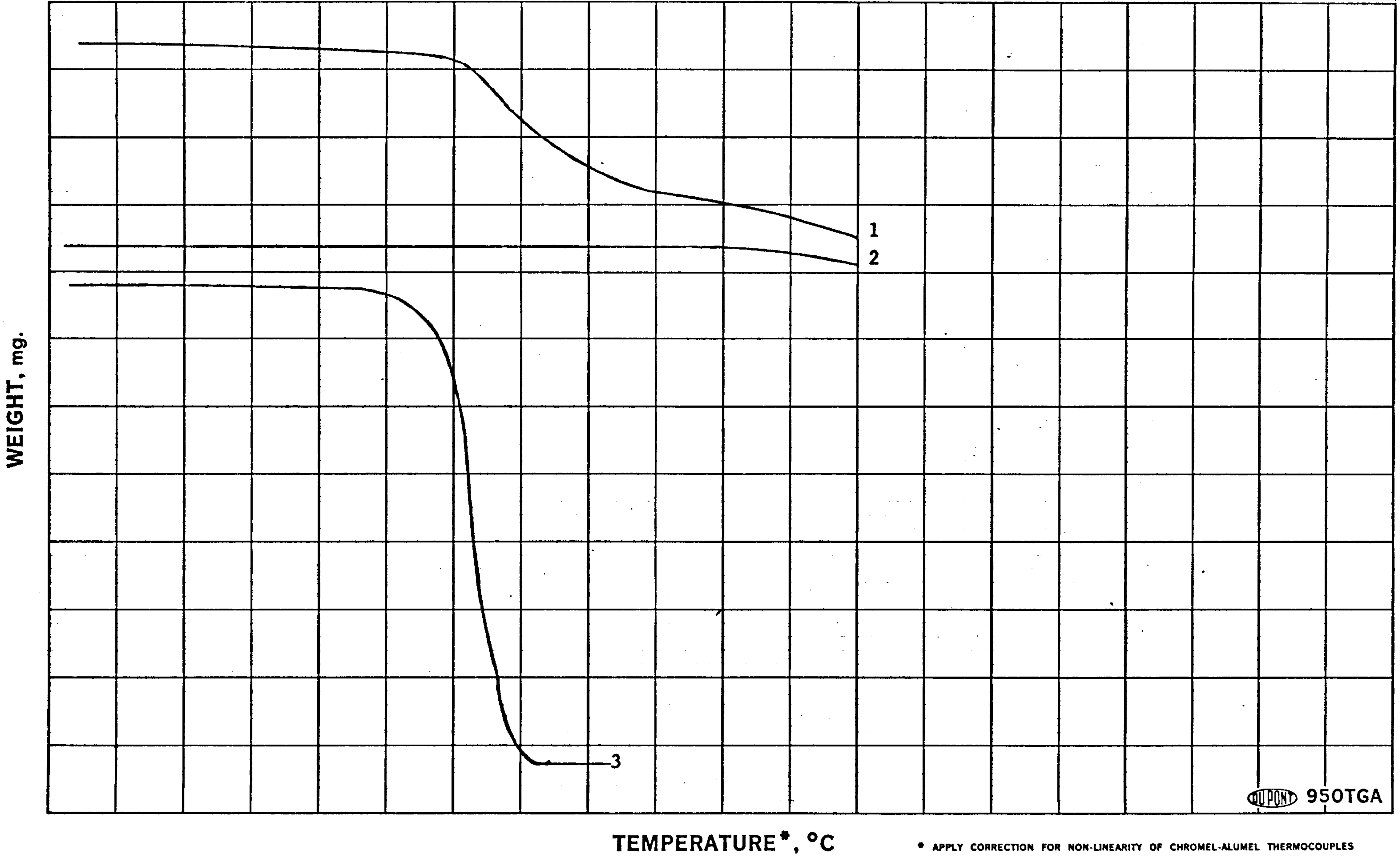
X-AXIS

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 8-21-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. (1) N_2, (2) N_2, (3) air
TIME CONSTANT 2 sec.

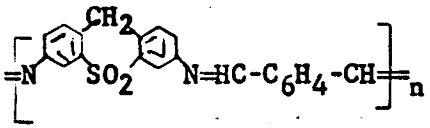


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 42

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

SAMPLE: DA-42-11



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.

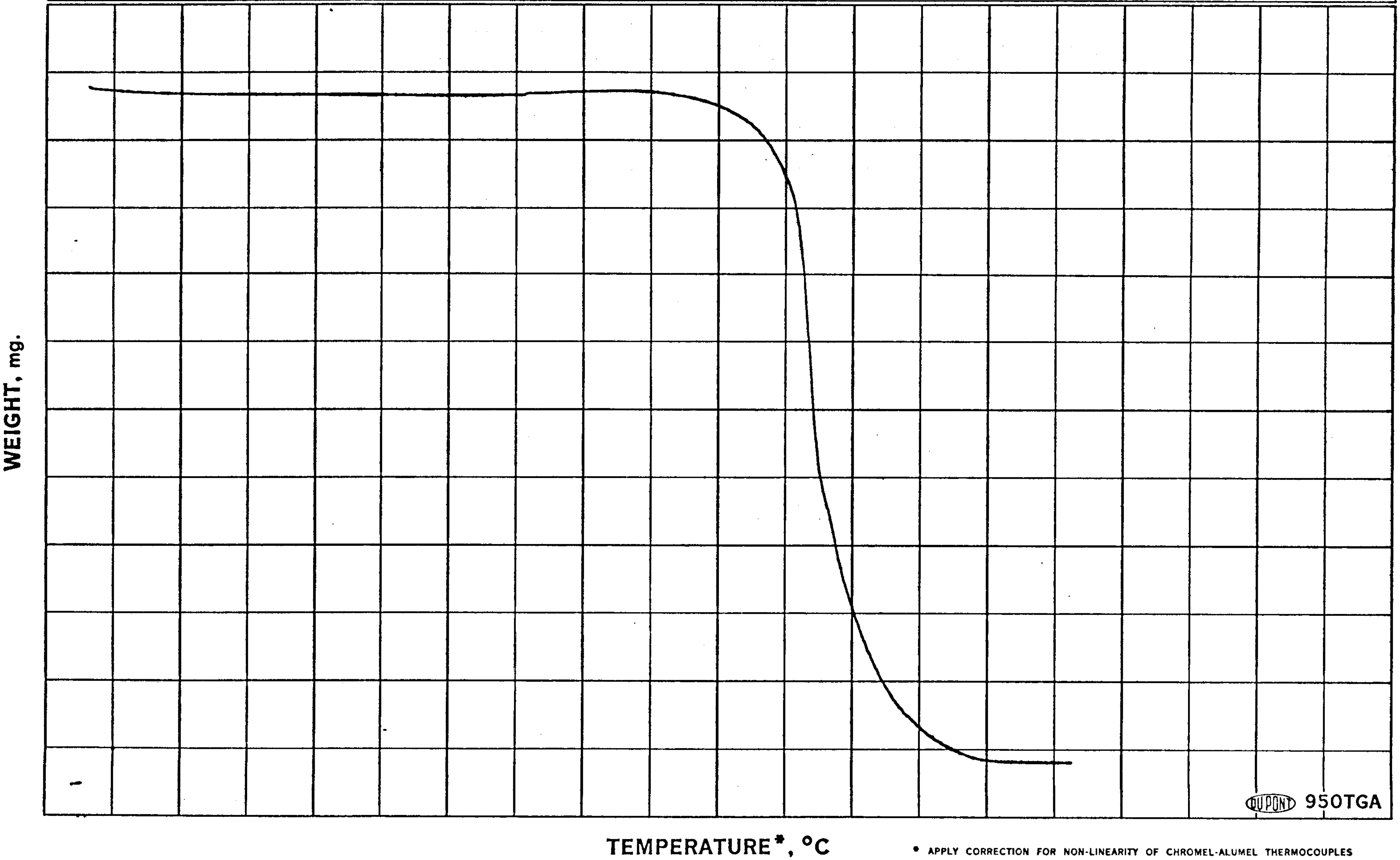
RUN NO. ____ DATE 8-20-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. air

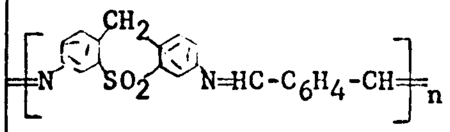
TIME CONSTANT 2 sec.



* 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-42-11-H600



SIZE 10 mg.

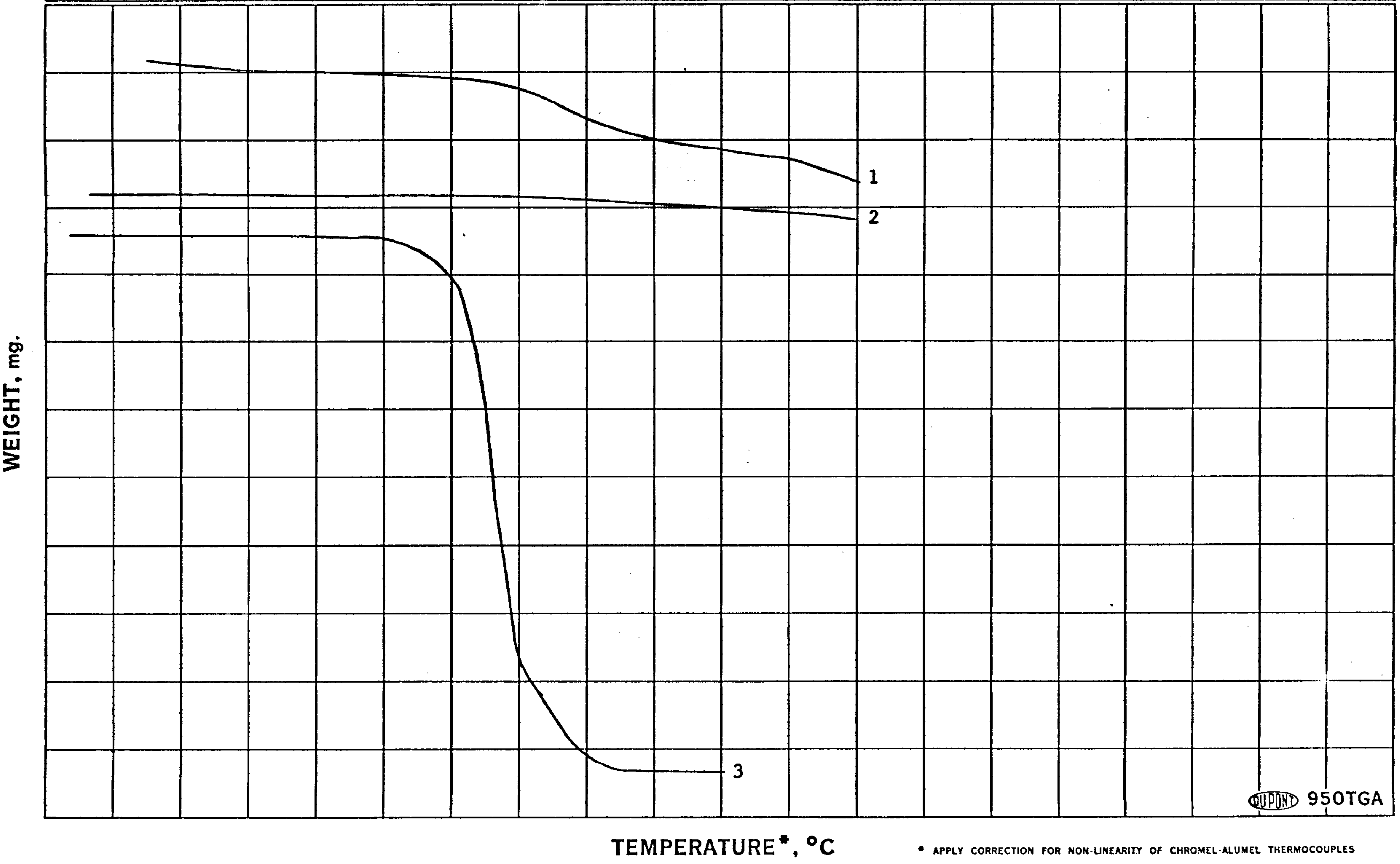
X-AXIS

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.

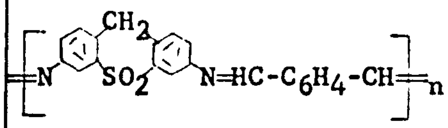
RUN NO.
DATE 9-14-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. (1) N_2, (2) N_2, (3) air
TIME CONSTANT 2 sec.



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

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-42-11-H600



SIZE 9.9 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.

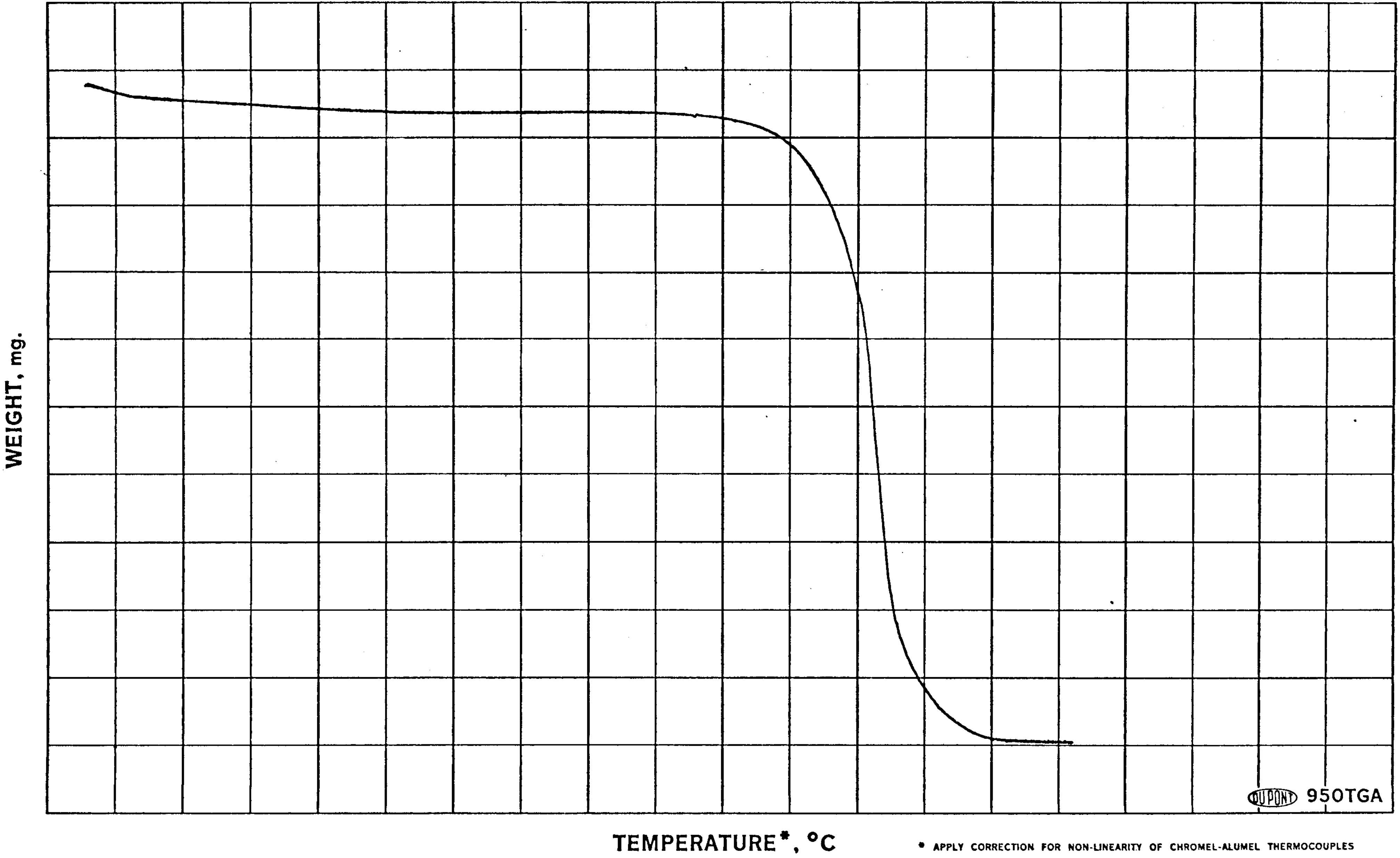
RUN NO. DATE 8-21-65

OPERATOR JVC

HEATING RATE 15 °C/min.

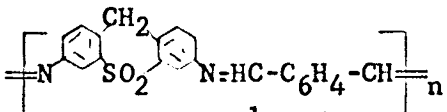
ATM. air

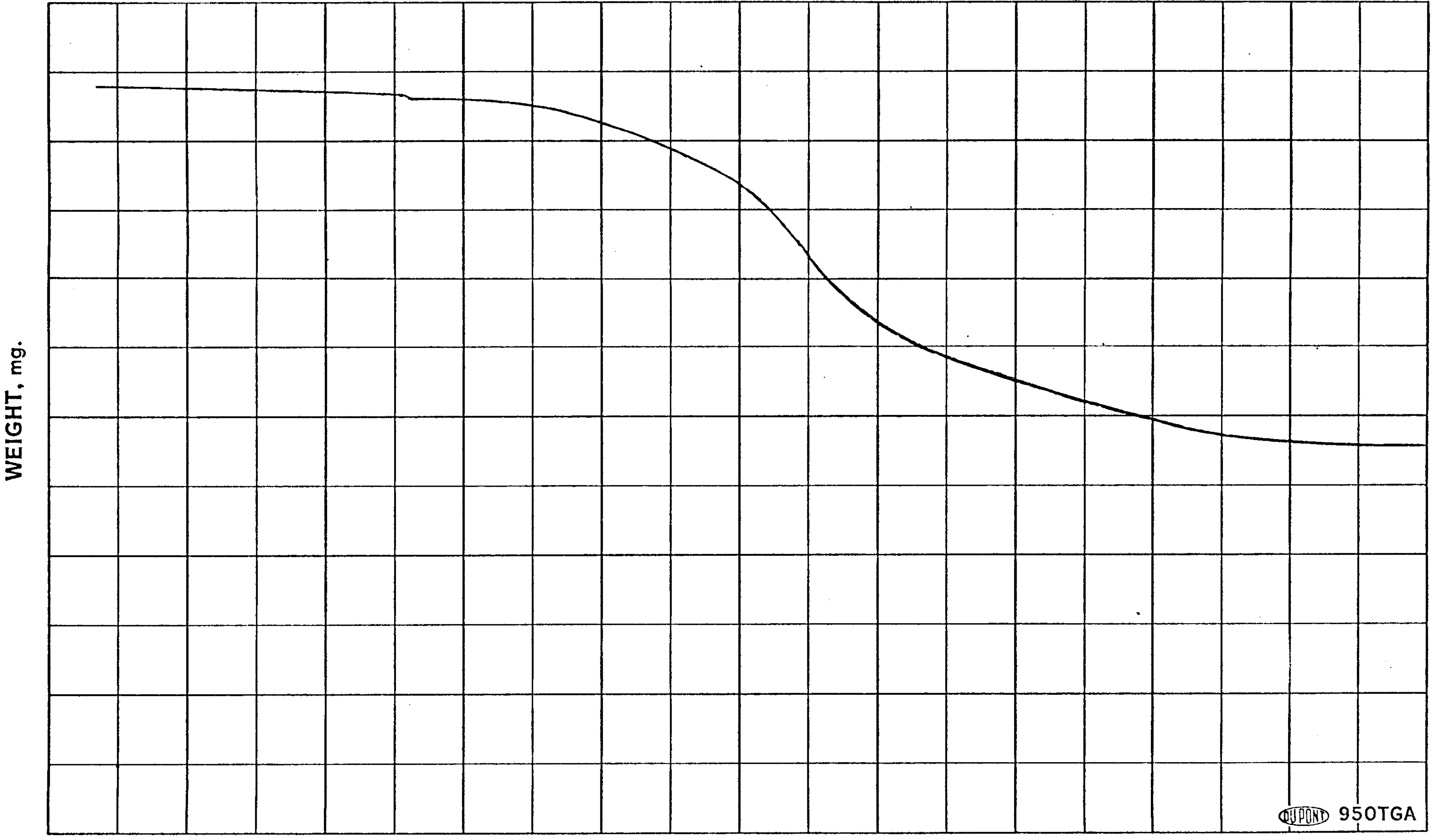
TIME CONSTANT 2 sec.



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

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

SAMPLE: DA-42-6  green polymer 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 8-19-65 OPERATOR JVC HEATING RATE 15 °C/min. ATM. nitrogen TIME CONSTANT 2 sec.



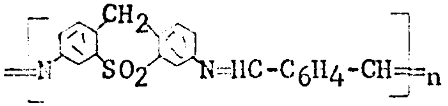
TEMPERATURE*, °C

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

Appendix No. 46

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

SAMPLE: DA-42-6



green polymer

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.

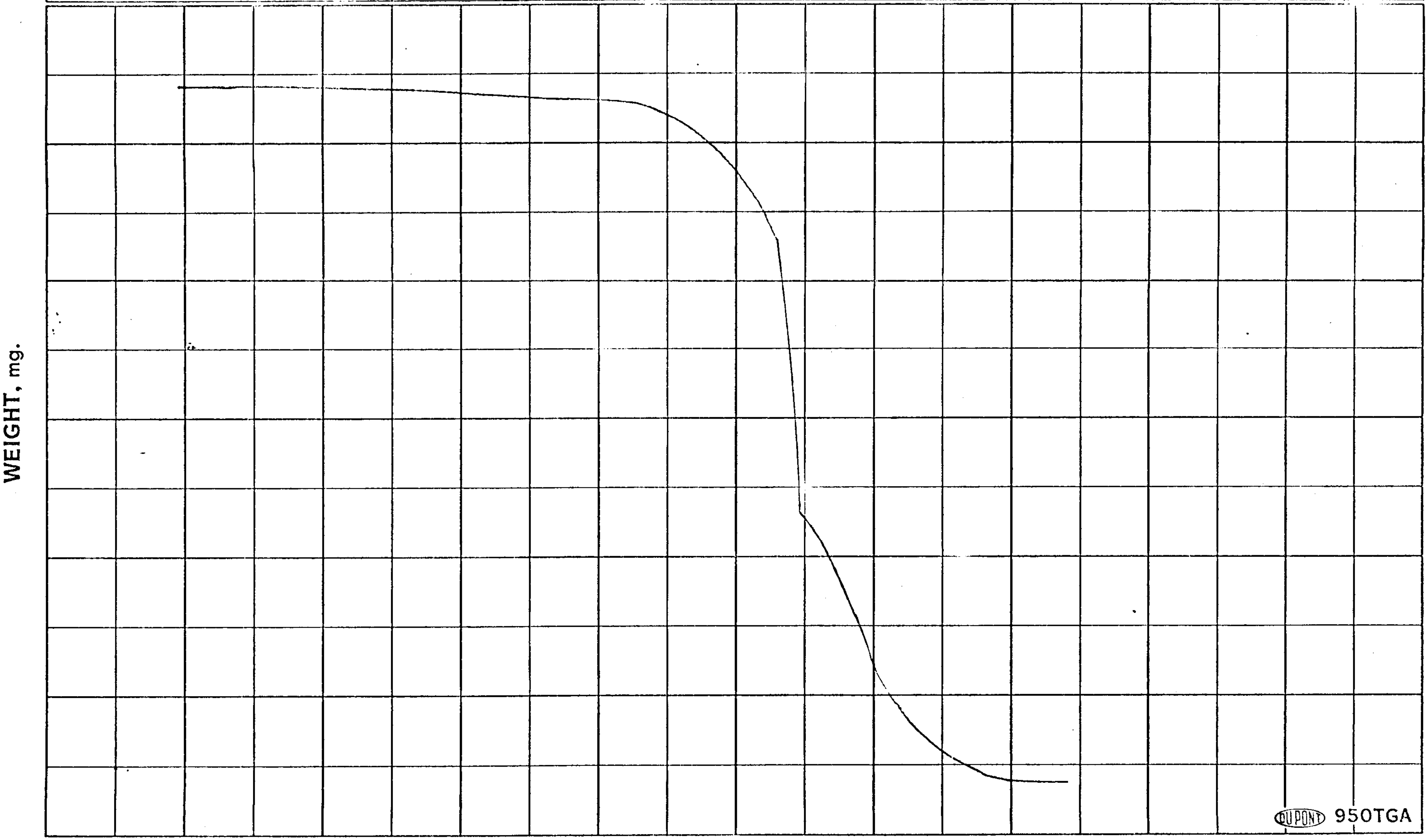
RUN NO. ______ DATE 8-17-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. air

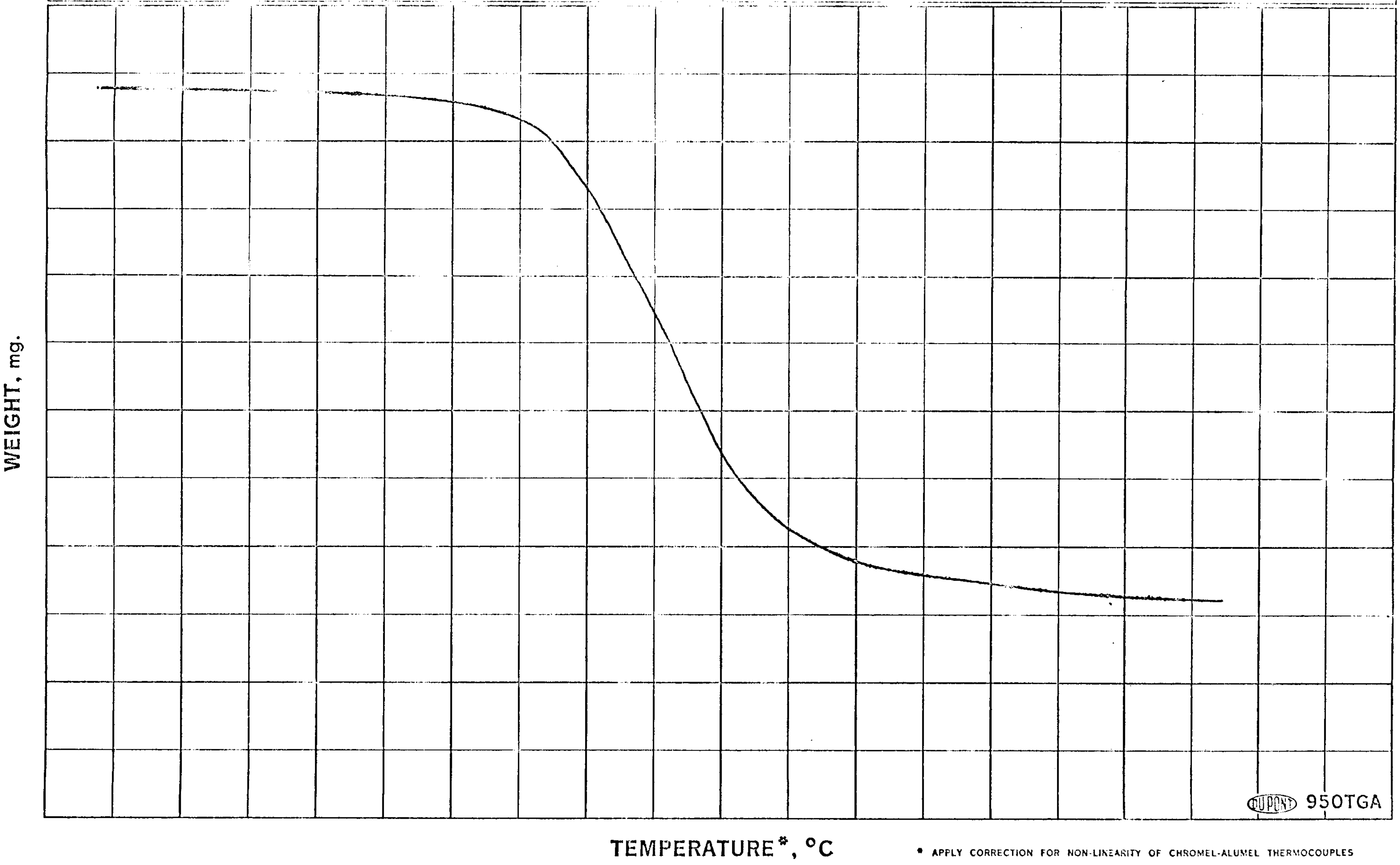
TIME CONSTANT 2 sec.



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

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

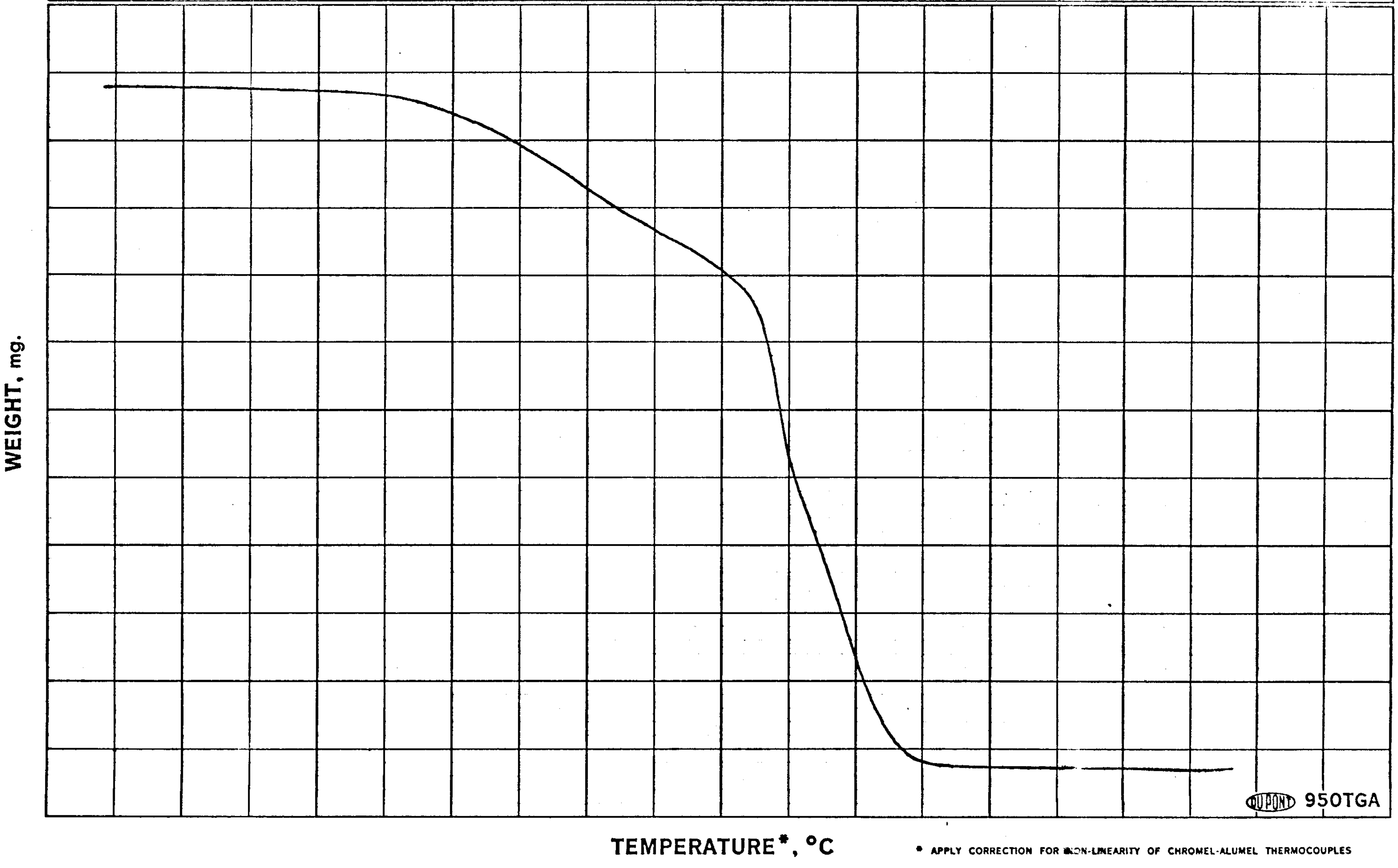
SAMPLE: DA-29-286	X-AXIS	Y-AXIS	RUN NO. ____ DATE 7-20-65
$\{N{=}(CH_2)_4{-}N{=}HC{-}C_6H_4{-}CH\}_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch	OPERATOR JVC
orange polymer	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C/min.
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	ATM. nitrogen
			TIME CONSTANT 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-29-286	X-AXIS	Y-AXIS	RUN NO. ______ DATE 7-20-65
$\{N-(CH_2)_4-N=HC-C_6H_4-CH\}_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch	OPERATOR JVC
orange polymer	SHIFT 0 inch	(SCALE SETTING X 2)	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

Du Pont INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-29-269

$\left[N\text{-}(CH_2)_4\text{-}N{=}HC\text{-}C_6H_4\text{-}CH\right]_n$

white polymer

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.

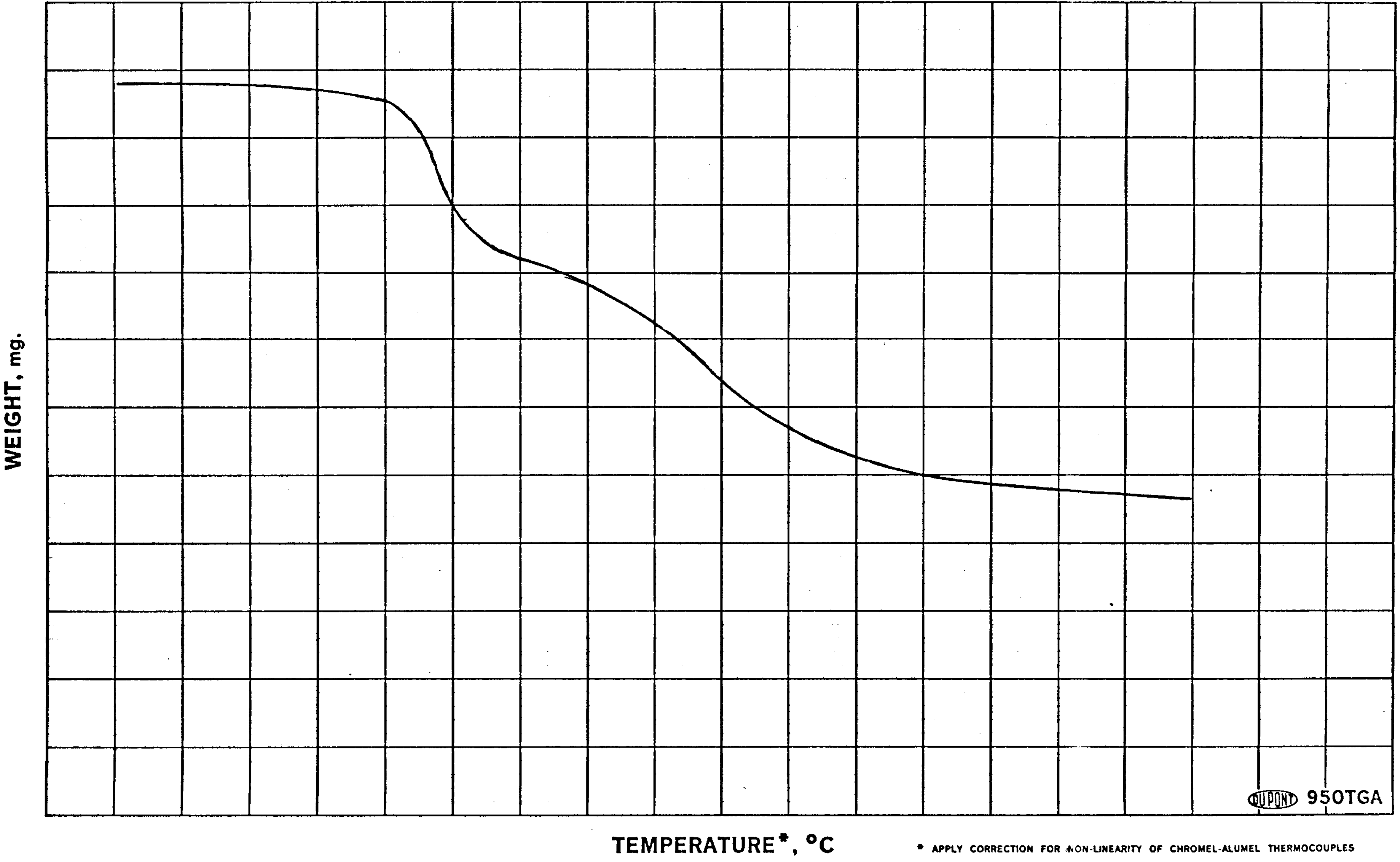
RUN NO. ______ DATE 7-13-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. nitrogen

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-29-269	**X-AXIS**	**Y-AXIS**	**RUN NO.** ____ **DATE** 7-26-65
$\{N-(CH_2)_4-N{=}HC-C_6H_4-CH\}_n$	**TEMP. SCALE** 100 °C/inch	**SCALE** 2 mg./inch	**OPERATOR** JVC
white polymer	**SHIFT** 0 inch	(SCALE SETTING X 2)	**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

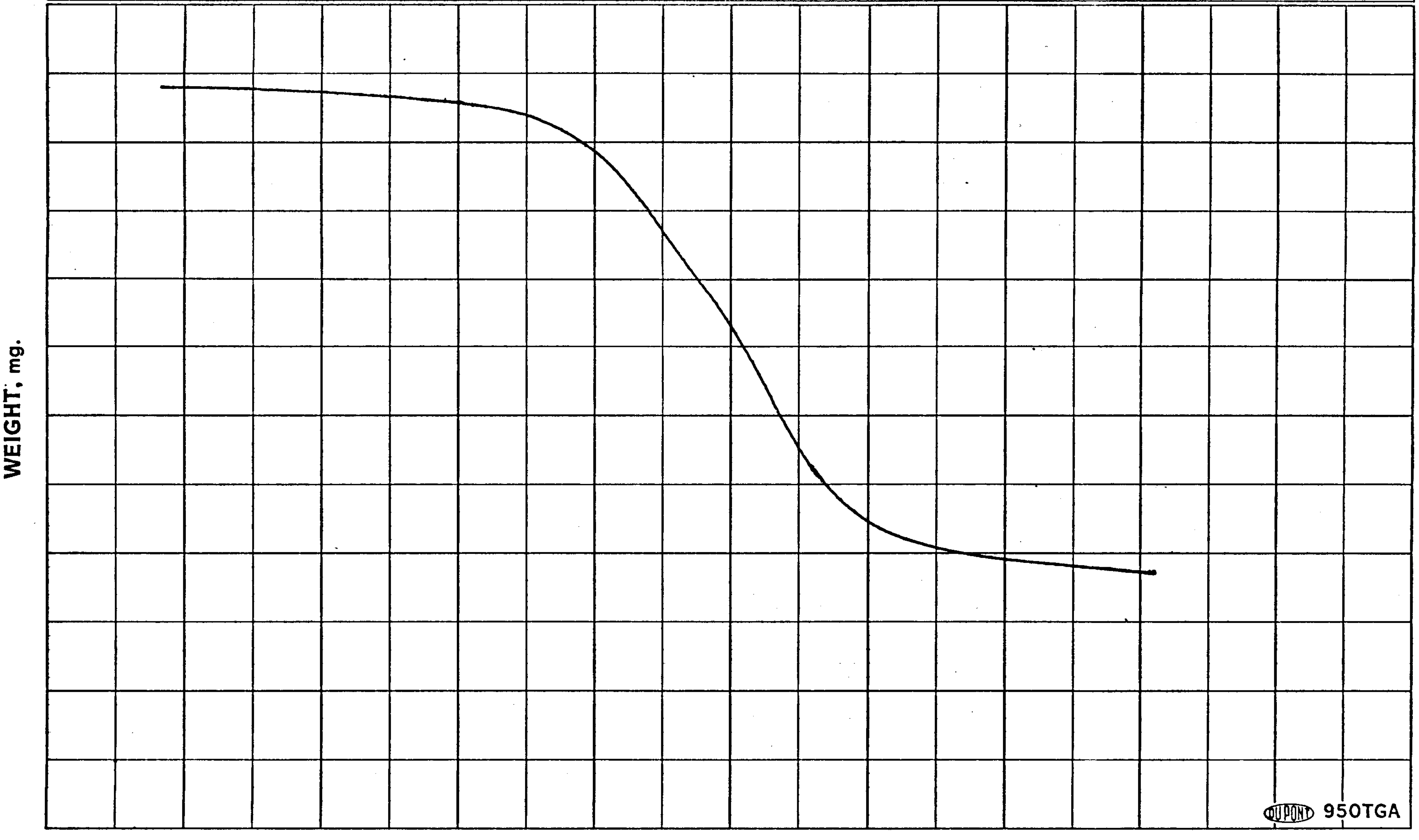
DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-42-10
$\{N\text{-}(CH_2)_6\text{-}N{=}HC\text{-}C_6H_4\text{-}CH\}_n$
orange polymer
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 8-19-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. nitrogen
TIME CONSTANT 2 sec.



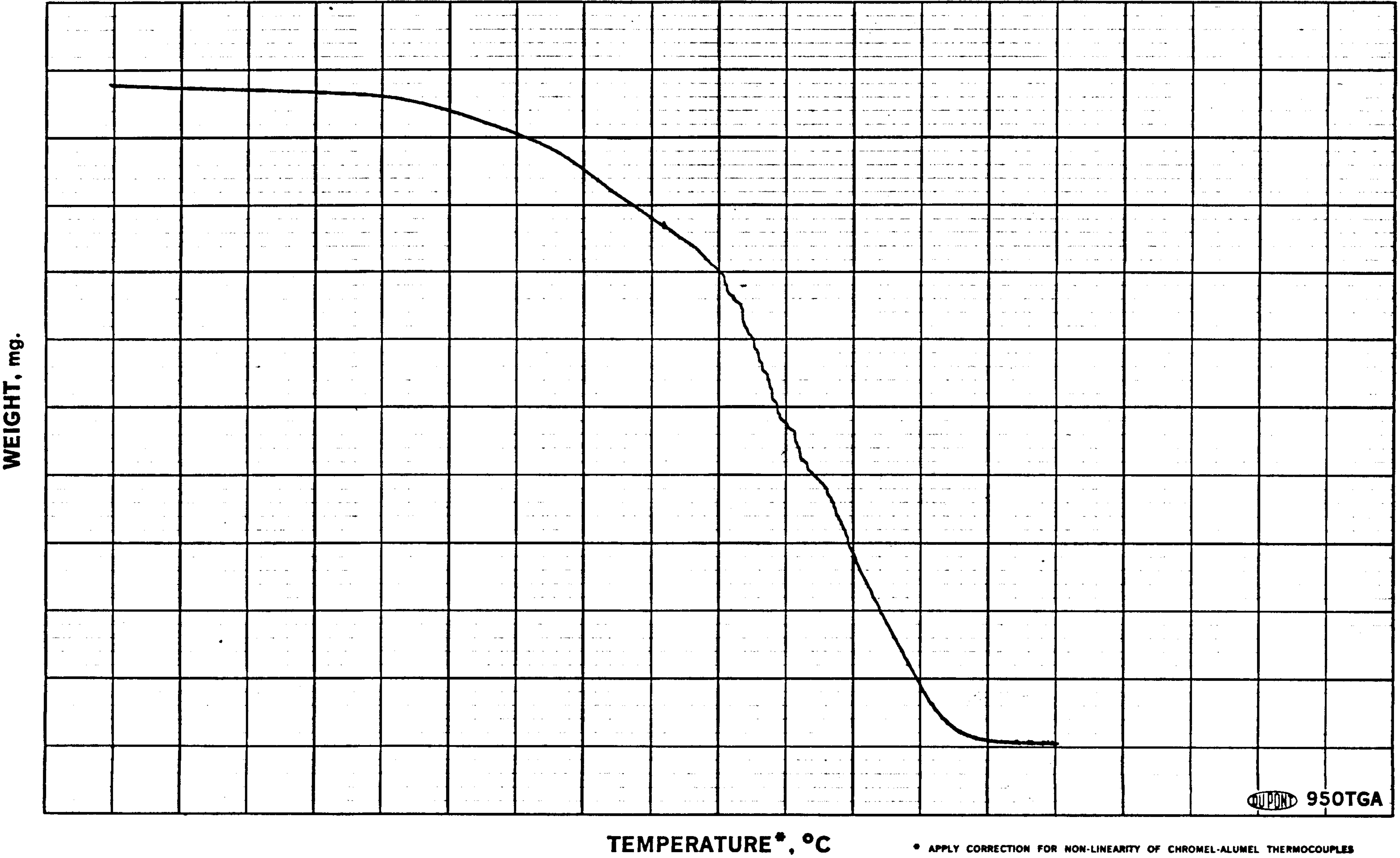
TEMPERATURE*, °C

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

PART NO 950017

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

SAMPLE: DA-42-10	**X-AXIS**	**Y-AXIS**	RUN NO.____ DATE 8-19-65
$\left[N-(CH_2)_6-N=HC-C_6H_4-CH \right]_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch	OPERATOR JVC
orange polymer	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C/min.
SIZE 9.8 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	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-29-268
$\{N-(CH_2)_6-N=HC-C_6H_4-CH\}_n$
white polymer
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 7-13-65
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-29-268	X-AXIS	Y-AXIS	RUN NO. ____ DATE 7-26-65
$\{N-(CH_2)_6-N=HC-C_6H_4-CH\}_n$	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR JVC
white polymer	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. 54

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

SAMPLE: DA-29-154

$\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$

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.

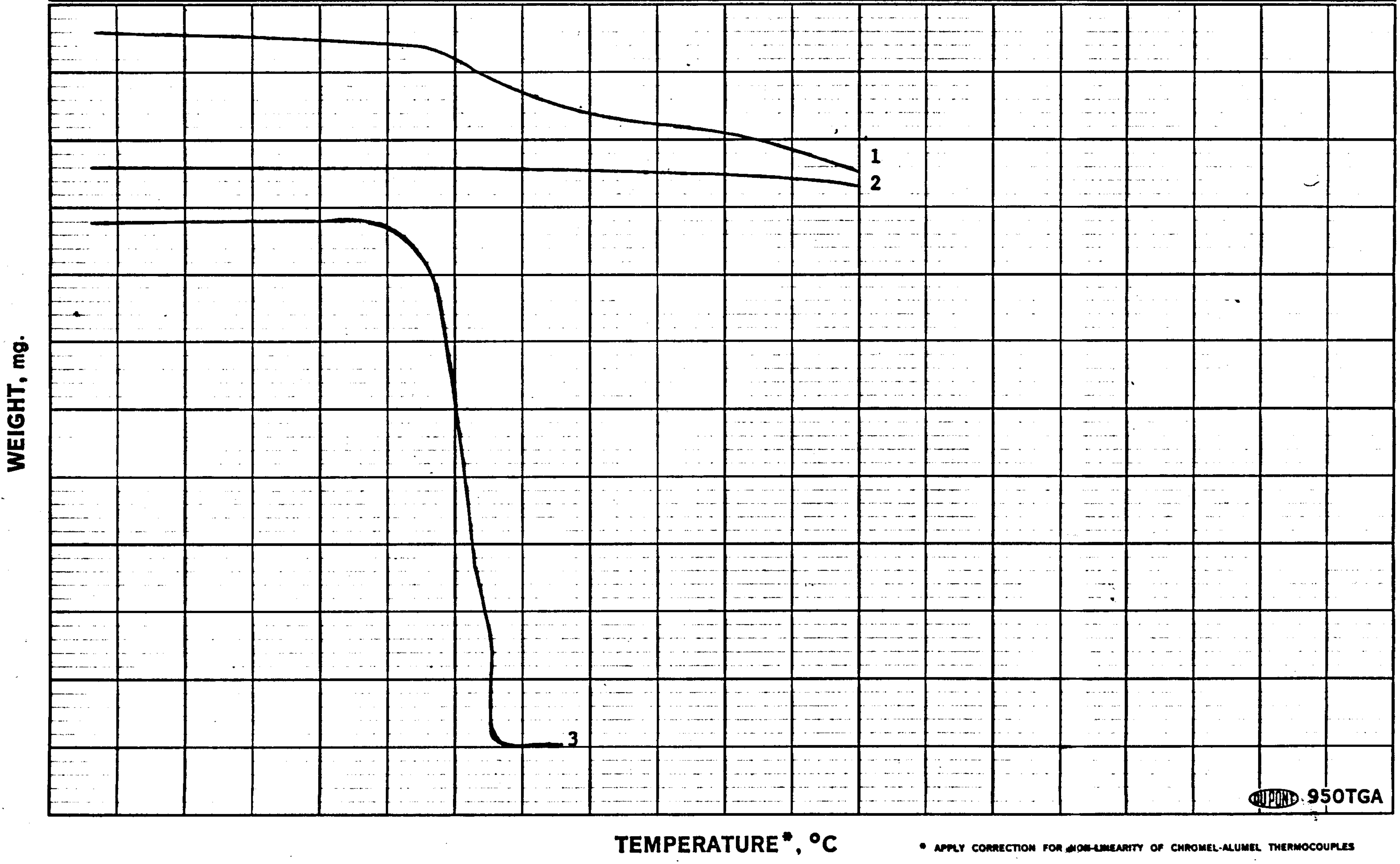
DATE 7-21-65

OPERATOR JVC

HEATING RATE 15 °C/min.

ATM. (1) N_2, (2) N_2, (3) air

TIME CONSTANT 2 sec.



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

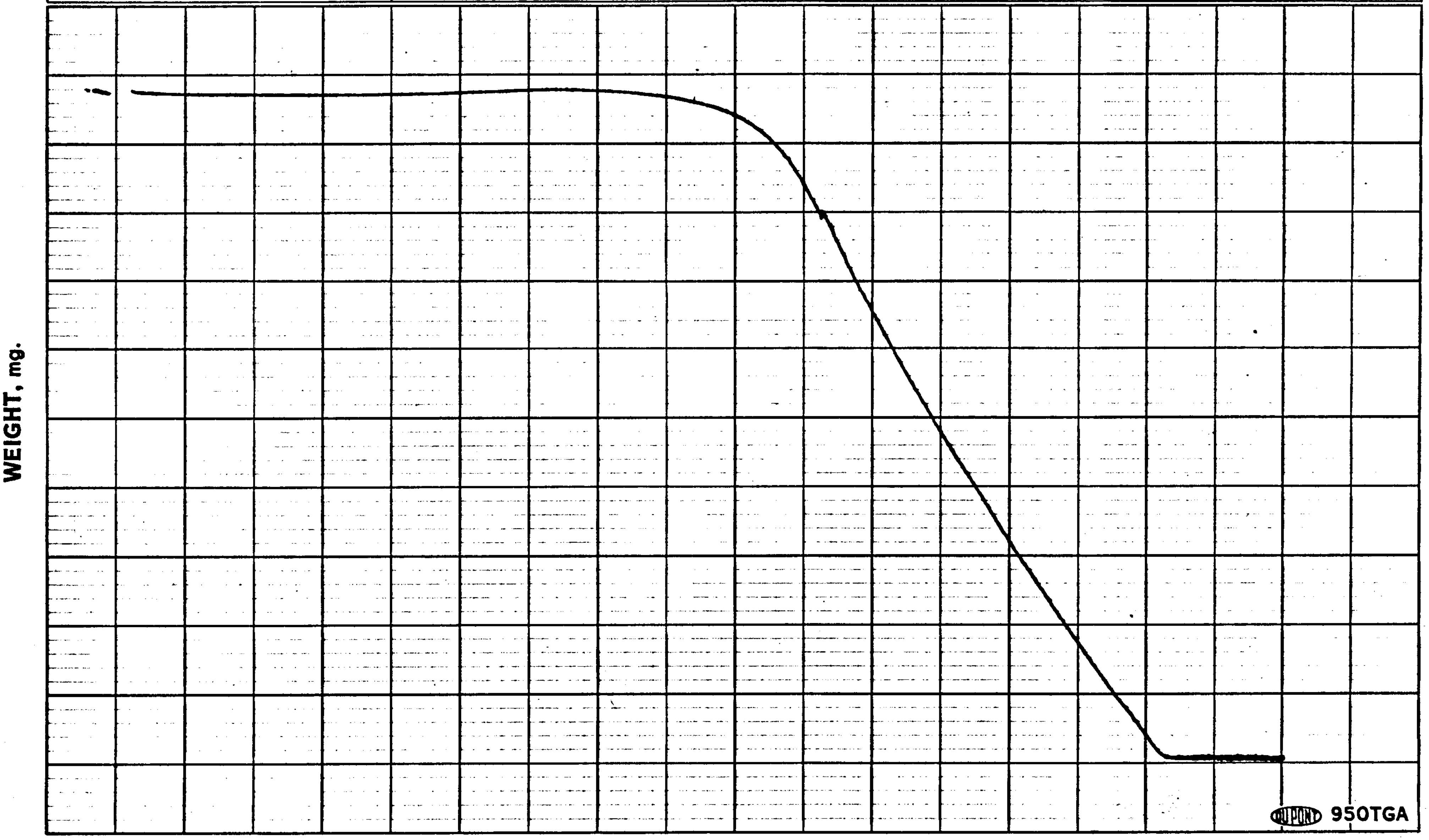
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-29-154
$\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$
SIZE 9.8 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 7-14-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



TEMPERATURE*, °C

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