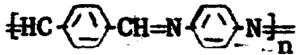
PROGRESS REPORT NUMBER 9

ON THE

FUNDAMENTAL STUDIES ON THE SYNTHESIS OF HEAT-RESISTANT POLYMERS

SOME PARAMETERS IN THE EVALUATION OF THE THERMAL STABILITY OF POLY(p-XYLYLIDENE-p-PHENYLENEDIAMINE), 

PERFORMED

UNDER

NASA GRANT NsG339

BY

G. F. D'ALELIO

N66 21780

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA 46556

FEBRUARY 15, 1966

FOREWORD

This report is a summary of the research performed under NASA Grant NsG339 for the period 15 September 1965 to 31 January 1966 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.

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

This report covers studies performed by G. F. D'Alelio, J. Crivello and T. Dehner.

Date February 15, 1966

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

ABSTRACT

21780

The substitution of helium for nitrogen in TGA measurements yield substantially the same values for the thermal stability of poly(p-xylylidene-p-phenylenediamine). This polymer shows high thermal stability in 100% oxygen.

The respective thermal stability values in nitrogen and in air are unchanged over a fourfold change in gas-flow rate or changes in heating rate over the range of 5°C to 30°C per minute. Higher apparent thermal stabilities are observed when the polymer sample of 10 milligrams is evaluated as a single mass rather than as a powder of approximately 500 pieces.

Infrared spectral studies confirm the Schiff-base character of the polymer and that heating to 600°C causes chain extension. Mass spectral studies of the products derived from heating the polymer to temperatures above 600°C show the products of the fragments of eliminated benzylideneaniline and hydrogen; the latter is the major product. The presence of hydrogen and other changes in the infrared spectra can be explained by the formation of ladder-type structures in the polymer. Calorimetric measurement of the Schiff-base polymer heated to 1000°C were compared to similar measurement of pyrolytic graphite and the conclusion made that graphitization has not occurred in the polymer.

A comparison of the thermograms before irradiation and after irradiation of the Schiff-base polymer exposed in either vacuo at 10^{-6} torr or open to air to a dosage of 200 megareps indicate that they are highly resistant to irradiation.

TABLE OF CONTENTS

Page

I Introduction-- 1

II Studies Involving Changes in Parameters-------------------- 4

A. General Experimental Procedure------------------------- 4

1. Nature of Inert Atmosphere--------------------------- 4

2. Nature of Reactive Atmosphere------------------------ 5

3. The Flow Rate of the Gaseous Atmosphere-------------- 6

a. Variations in Flow Rates in Nitrogen--------------- 7

b. Variations in Flow Rate of Air--------------------- 7

4. Variations in the Heating Rate----------------------- 8

5. Variations in Particle Size of Sample---------------- 11

III Evidence for Changes in Polymers as a Result of Heating----- 12

A. Infrared Measurements------------------------------------ 12

B. Mass Spectral Analyses---------------------------------- 15

C. Calorimetric Studies------------------------------------ 18

1. Cell Constant-- 18

2. Behavior of Polymer DA-42-13------------------------ 18

a. In Nitrogen-- 19

b. In Air--- 19

3. Behavior of Polymer Post-Heated to 1000°C------------ 20

4. Behavior of Pyrolytic Graphite----------------------- 22

IV Stability of Schiff Base Polymers to Ionizing Radiation----- 23

A. Polymer Irradiated at Reduced Pressure------------------ 25

B. Polymer Irradiated After Sealing in Air Atmosphere------- 25

C. Polymer Irradiated While Exposed to Air----------------- 26

Page

V Summary and Conclusions------------------------------------ 26

VI Future Work-- 28

VII Bibliography--- 30

VIII Acknowledgment--- 31

IX Appendix---

I. Introduction.

In a previous study,[1] values expressing the thermal stabilities of a number of Schiff base polymers were reported. These values were derived from thermograms obtained with du Pont 950 Thermogravimetric.Analyzer.

The ability of the thermogravimetric and thermodifferential methods of analysis to determine the thermal properties of materials is well known.[2-4] These two methods are usually employed as complimentary sources of data, and together indicate precisely the temperatures at which degradations and phase changes occur.[5]

A number of our preliminary studies showed that the inflections of the thermogravimetric curves, and hence, the data derived from them, were dependent to some measure on a number of parameters. Variations in the heating rate, environmental gas flow rate and particle size were responsible for some shifts in the thermogravimetric curves.

A review of the literature[6-8] also shows no general acceptance of standardized conditions or values for these parameters; indeed, in many cases all parameters are not specified.

It was necessary, therefore, in the previous report[1] to specify these parameters, and, in order to facilitate comparisons among the various polymers, to adopt specific values to be used uniformly for all the samples examined. The conditions used were:

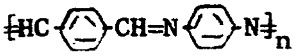
1. a heating rate of 15°C per minute;
2. a gas flow rate of one (1) standard liter per minute;
3. 10 mg. samples composed of particles whose sizes were specified by the grinding conditions;
4. a grinding time of fifteen seconds in a stainless steel grinding capsule.

The temperatures recorded were corrected for the non-linearity of the chromel-alumel thermocouples. The thermogravimetric determinations were performed in nitrogen and in air to determine both the "true" and "practical" thermal stabilities.

There does not appear to be in the literature general agreement on how to assign thermal stability values from the thermogravimetric analysis curves. Various schemes have been proposed, such as the "differential procedural decomposition temperature" and the "integral procedural decomposition temperature," which give decomposition temperatures based on the areas under the thermogravimetric curves.[9] While these methods give values which can be compared and evaluated, there seems to be some doubt as to the real significance of the data. Other researchers[10,11] base their evaluation of thermal stability on comparisons among the thermogravimetric curves themselves.

In our early report,[1] the latter approach[10,11] was taken. Data was abstracted from the curves and placed in tabular form to facilitate analysis and comparison. Thus, tables were assembled which summarized the data in the following categories: per cent weight losses at various temperatures; temperatures of specific per cent weight losses; and temperatures of inflection corresponding to the onset of decomposition or further reaction. The temperatures of inflection were obtained from (1) the intersection of the slope of the curve before a negative change in slope has occurred and (2) the slope of the curve at maximum decomposition.

Since the limits of the parameters were chosen arbitrarily,[1] it was considered important to reexamine the parameters which were used to establish the thermal stability values assigned to the Schiff base polymers, and to determine what effect, if any, changes in the parameters would have on the thermal stability values assigned. As part of these new studies, measurements were to be made also to attempt to determine the changes which take place in a Schiff base polymer when it is heated to high temperatures.

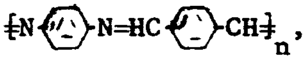
The polymer, poly(p-xylylidene-p-phenylenediamine),  was selected for these studies. In previous TGA measurements,[1] nitrogen had been used as the inert environmental gas. Since the question could be raised as to whether or not nitrogen reacted with the polymers at high temperature, a comparison was made between nitrogen and helium in these new studies. Also, air had been used[1] as the reactive gas, and the high thermal resistance of the polymers in air, suggested that 100% oxygen should be contrasted with air. Further, the flow rate of the gaseous atmosphere, one standard liter per minute, was used[1] previously. In these new studies, nitrogen and air were reevaluated over a range of flow rates. In addition, since surface area changes vary greatly with particle size, it was considered necessary to evaluate the thermal stability of the polymers over a range of particle sizes.

Since thermal treatments of polymers can produce changes in their structures, studies were included which would give evidence of these changes. Infrared, mass spectral and calorimetric measurements were made to gain some insight into these changes. The calorimetric studies were directed to obtaining ΔH values of the polymer in nitrogen and in air in an attempt to resolve the question as to whether or not the Schiff base polymers are "graphitized" when heated in an inert atmosphere to high temperatures. Accordingly, a comparison was made with pyrolytic graphite. The high thermal stability of the polymers led to studies to determine the stability of the polymeric Schiff bases to ionizing radiation; this was to be done by comparing the thermogravimetric curves before and after exposure to the radiation.

II. Studies Involving Changes in Parameters.

A. General Experimental Procedure.

These studies were performed on a du Pont Thermogravimetric Analyzer in conjunction with a 900 Differential Thermal Analyzer. To facilitate comparisons among the various samples, sample weights of 10 mg. were used in most determinations and the instrument was set to a sensitivity of 2 mg. per inch with a time response of two seconds. A temperature correction has been made in these determinations for the non-linearity of the chromel-alumel thermocouple.

The polymer, DA-42-13, , was considered to be typical of the conjugated and pseudoconjugated Schiff base polymers and was selected to be representative of these polymers in the study of the parameters which could influence the determination of the thermal stability values.

1. The Nature of the Inert Atmosphere.

Many of the determinations described in the previous report[1] were performed in an atmosphere of dry nitrogen. The nitrogen used in these studies was a high purity lamp grade obtained from the Cleveland Wire Division of the General Electric Company. This gas was presumed to be inert and thus, the thermal stabilities determined in this gas were presumed to reflect the "true" thermal stability, that is, the thermal stability based on the strengths of the bonds between the atoms. However, the question arose as to the actual non-reactivity of nitrogen at high temperatures, especially in the region above 1000°C. It is possible that at these temperatures nitrogen may be reactive enough to attack the polymer structure and thus, to contribute either to a loss in weight by degradation or to an increase in weight by addition.

To adequately evaluate the possible effect of nitrogen at high temperatures in these polymer systems, it was necessary to determine their thermal stability in an atmosphere which has been shown to be inert. Helium and argon, being inert gases, would be expected to be non-reactive even at the high temperatures employed in these studies. Thus, a sample of polymer DA-42-13 was thermoanalyzed in helium to 1176°C and its thermogram compared with the thermograms of the same polymer thermoanalyzed in dry nitrogen. The composite thermogram is shown in Appendix No. 1.

A comparison of the thermogravimetric plots show little difference either in the shape of the thermogravimetric curves or in the resulting weight losses. It follows thus, that nitrogen is non-reactive towards Schiff base polymers even at very high temperatures in excess of 1000°C. Nitrogen, therefore, may be considered an inert sample gas and the thermal stabilities determined in this atmosphere may be considered "true" thermal stabilities.

2. The Nature of the Reactive Atmosphere.

In the previous report,[1] a study was conducted to determine the thermal behavior of the Schiff base polymers in air as the active gas environment. In this case, active environment is defined as a medium which, because of its chemical reactivity aids the thermal degradation of the polymer. The thermal stabilities of the conjugated and pseudoconjugated polymers in this environment are very high[1] and are of the order of 500-600°C. Because of this high stability, it was of interest to determine the thermal stability of Schiff base polymers in a more active environment, particularly in pure oxygen. Accordingly, a thermogravimetric analysis was made using 100% oxygen; thermograms were recorded in this gas at the two different flow rates of 0.5 and 2.0 standard liters per minute. The two thermograms are shown in a composite chart as Appendix No. 2.

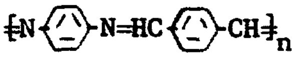
A brief analysis of these curves shows that polymer DA-42-13,  which has been condensed to 400°C, retains most of its thermal stability in oxygen as compared with air. Table 1 contrasts the relative thermal stabilities of polymer DA-42-13 thermoanalyzed in air (Appendix No. 3) with a flow rate of one (1) standard liter per minute with oxygen at 0.5 standard liter per minute and 2.0 standard liters per minute.

Table 1

Data From Thermoanalyses in Air and Oxygen

Atmosphere	Flow Rate Std l/min.	Point of Inflection °C	Appendix No. - Curve No.
Oxygen	0.5	447	2 - 1
Oxygen	2.0	488	2 - 2
Air	1.0	579	3

The thermogravimetric plots show two interesting features which result from the use of oxygen as a sample atmosphere. First, the negative slope indicating thermal degradation, is very steep suggesting that very rapid oxidative decomposition is taking place. Second, the curves show that during the thermoanalysis the sample temperature rises higher than the cell temperature, and thus, the samples are burning. Samples thermoanalyzed in air show a smooth oxidative decomposition and not a catastrophic and fast decomposition of the polymer sample.

From these studies it follows that, the thermal stability of black conjugated Schiff base polymers is influenced by the use of a very reactive atmosphere of pure oxygen, however, the thermal stability of these polymers in this environment remains about the same order of magnitude as in air.

3. The Flow Rate of the Gaseous Atmosphere.

Another parameter which must be considered in the evaluation of thermal stabilities is the gas-flow rate of the sample atmosphere. When slow gas-flow rates are used, hot gaseous products arising from the thermal degradation of the sample remain in the immediate vicinity of the polymer. Combustion of these products may raise the temperature of the sample and aid in its decomposition. If faster flow rates are used, these degradation products are removed as they are formed and thus, do not contribute to thermal degradation.

A sample gas flow rate of one standard liter per minute was used in the previous studies[1] and was regarded as adequate to sweep most of the degradation products away from the main polymer sample. This gas flow rate was the value recommended by the du Pont Company for general use in thermoanalysis in their 950 Thermogravimetric Analyzer.

In these new studies, gas-flow rates of 0.5 and 2.0 standard liters per minute were employed to assess the effect of higher and lower gas-flow rates on thermoanalyses of Schiff base polymers. The variation in flow rates was used for studies in two sample atmospheres, air and nitrogen.

a. Variations in Flow Rates of Nitrogen.

Two samples of polymer DA-42-13 were thermoanalyzed in nitrogen, one at a gas-flow rate of 0.5 standard liter per minute and the other at 2.0 standard liters per minute. The composite thermograms are shown in Appendix No. 4.

The thermograms show little variation due to changes in gas-flow rate and are almost identical in all details. It may be concluded, therefore, that within the limits of this experiment, the thermal stability in nitrogen is not appreciably changed over a fourfold change in gas-flow rate.

b. Variations in the Flow-Rate of Air.

Two samples of polymer DA-42-13 were thermoanalyzed in air, one at a gas-flow rate of 0.5 standard liter per minute and the other at 2.0 standard liters per minute. The thermograms are shown in Appendix No. 5

Examination of these thermograms indicates that there is only a very small effect which results from a fourfold variation in the gas-flow rates in air. Hence, in these studies of Schiff base polymers, the gas-flow rate plays only a very minor role in the total assessment of their thermal stability.

4. Variations in the Heating Rate.

The thermal stability of polymers is based not only on the extremes of environmental conditions which it can withstand, but also upon the duration of exposure to such conditions. Various researchers have adopted a wide variety of heating rates in the evaluation of their polymers. Heating rates from 30°C per minute to 150°C per minute have been used to determine thermal stabilities. In the previous report[1] a standard heating rate of 15°C per minute was adopted and used throughout the determinations.

It is recognized, that thermal stabilities of different polymers determined at different heating rates cannot be easily compared. Thus, it was desirable to perform several thermoanalyses at different heating rates to determine the magnitude of effect of this parameter on the thermal stability of Schiff base polymers.

In this study, the polymer, poly(p-xylylidine-p-phenylenediamine), DA-42-13, was thermoanalyzed in nitrogen, recycled again in nitrogen, and then recycled in air. The heating rates chosen in this study were 5 and 30°C per minute. A composite thermogram showing both sets of data are shown in Appendix No. 6 and are plotted close to one another to facilitate comparisons. The thermograms clearly show the expected results. When the heating rate is slow, as in the case where 5°C per minute was used, the overall thermal stability of the polymer is lower than when the heating rate is six times faster, that is, when the heating rate is 30°C per minute.

Table 2 contrasts the data obtained from the thermoanalysis of polymer

DA-42-13, in nitrogen at heating rates of 5, 15, and 30°C per minute.

Table 2

Per Cent Weight Loss in Polymer DA-42-13 While
Being Heated in Nitrogen at Various Heating Rates

Heating Rate °C	Per Cent Weight Loss at °C										Appendix Number
	300	400	500	600	700	800	900	1000	1100	1176	
5	0.4	1.2	2.8	9.0	17.6	21.0	22.0	23.8	28.2	29.2	6
15	0.0	1.2	2.4	10.0	18.4	22.0	23.4	24.4	26.6	29.4	3
30	0.0	0.4	1.7	5.4	15.0	18.4	20.4	20.8	22.6	25.0	6

The data contained in this table shows that there is very little difference in the weight losses obtained at the two lower heating rates, 5 and 15°C per minute. However, when the heating rate is increased to 30°C per minute, the polymer shows lower weight losses and hence, a slightly higher thermal stability. For example, the resulting weight loss at 1176°C with a heating rate of 30°C per minute is approximately 4% less than with heating rates of 5 and 15°C per minute.

Table 3 summarizes the data obtained from recycling the polymer in nitrogen at heating rates of 5, 15, and 30°C per minute.

Table 3

Per Cent Weight Loss in Polymer DA-42-13 While
Recycling in Nitrogen at Various Heating Rates

Heating Rate °C/min.	Per Cent Weight Loss at °C					Appendix No. - Curve No.
	800	900	1000	1100	1176	
5	1.0	1.1	1.2	3.2	6.0	6 - 2
15	0.2	0.6	1.0	1.8	2.6	3 - 2
30	0.6	0.6	0.6	0.8	1.2	6 - 2'

It is apparent that the greatest weight losses occur on recycling in nitrogen when the slowest heating rate is used. The weight loss in this case (5°C per minute) is five times greater (6%) than when the fastest heating rate (30°C per minute) (1.2%) is used. It is also interesting to note that, the major portion of this weight loss at the slowest heating rate occurs within the last two hundred degress, and that, up to 1000°C the curves for both heating rates are essentially identical.

The greatest effect of a variation in the heating rate on the thermal stability would be expected to take place in an active atmosphere. In this case, the polymer would be subjected to chemical attack for longer periods of time at the lower heating rates, and thus, should show higher weight losses for the same temperature than at higher heating rates. Such a result is observed in polymer DA-42-13 in air after first recycling in nitrogen. The data obtained from curve 3 and 3' of thermogram shown in Appendix No. 6 is summarized in Table 4.

Table 4

Temperatures of Inflection of Polymer DA-42-13 in Air After Recycling in Nitrogen at Various Heating Rates

Heating Rate °C/min.	Temperature of Inflection °C	Appendix No. - Curve No.
5	570	6 - 3
15	580	3 - 3
30	588	6 - 3'

The thermograms and the data contained in this table show that oxidative degradation occurs earlier in those samples using slower heating rates. Also the curves obtained at slower heating rates show steeper slopes during the degradation indicating that the rate of decomposition may be higher in these cases.

Variations in heating rate thus, have been shown to produce some shifts in the thermal stability of Schiff base polymers. The magnitude of the difference in thermal stabilities, however, is not large, thus the values set forth in the previous report represent a realistic evaluation of the thermal stabilities of these polymers.

5. Variations in Particle Size of Sample.

Thermal stabilities are often reported in the literature without reference to the particle size of the samples examined by thermal analysis. That particle size is a parameter in the consideration of thermal stabilities appears reasonable since many degradative processes are partially dependent on the amount of surface area. For example, diffusion of degradative products generated within a powdered sample is very much more rapid than in a bulk sample. Accordingly, powdered samples would be expected to show greater weight losses in inert atmospheres than bulk samples. In active atmospheres, the chemical attack of the active agent is greatly dependent on surface area. Since powdered samples, possess very large surface areas when compared to bulk samples, they would be expected to exhibit lower thermal stabilities.

To evaluate particle size as a parameter, a study was conducted using 10 mg. samples of polymer DA-42-13 which had been reduced to widely differing particle sizes. A series of thermograms with different samples having the following number of particles per 10 mg.

a - 1 piece
b - 4 pieces
c - 22 pieces
d - 500 pieces

were performed in air and in nitrogen. These thermograms are shown as a composite in Appendix No. 7.

The thermograms show a progressive increase in weight loss as the particle size becomes smaller. In nitrogen, the bulk sample shows little or no weight loss up to 600°C, this is contrasted with about 500°C for the sample containing 500 pieces. A similar 100°C difference occurs when the samples are thermoanalyzed in air. In air, thermodegradation, in the bulk sample, begins at about 600°C while the sample containing 500 pieces starts to decompose at about 500°C. This data indicates that there is a marked dependency between particle size and thermostability. Accordingly, particle size must be specified in any determination of thermal stability and must be known before comparisons can be drawn between the thermal stabilities of various polymers.

It was for this reason that the thermoanalyses were performed[1] in the previous research using a specified sample preparation procedure; bulk samples, to be used for analysis, were ground for fifteen seconds in a stainless steel grinding capsule, to insure approximately 500 particles/10 mg.

III. Evidence for Changes in Polymers as a Result of Heating.

To determine changes in structure, verification of the original structure is required. Based on prototype and on unambiguous syntheses, the structure of the polymer obtained by Schiff base exchanges is unquestionably that of a poly Schiff base. However, at this time, it is desirable to obtain more concrete evidence for their structures. This would serve another purpose of this investigation, namely, to determine, at least in part, the effect of very high temperatures on the Schiff base structure.

Three different methods were used in these investigations of polymer structure; infrared spectroscopy: mass spectrometry; and differential thermal calorimetry.

A. Infrared Spectral Studies.

Infrared absorbtion spectroscopy was used in attempts to elucidate the structure of the Schiff base exchange polymers. Prominent bands were assigned spectral regions by the study of model compounds and of yellow low molecular weight polymers. The spectra were obtained from the potassium bromide discs using a Perkin-Elmer 421 Grating Spectrophotometer and are found in Appendix Nos. 8-14. The black, high molecular weight polymers, poly(p-xylylidene-p-phenylenediamine) (DA-42-13), and poly(p-xylylidene-m-phenylenediamine) (DA-42-14), were taken to be representative of the conjugated and pseudoconjugated polymers in general, and their spectra were studied. These spectra, shown in Appendix Nos. 15 and 16, proved to be rather simple and the bands very much broadened, as is generally observed in the spectra of polymers.

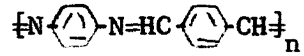
Two regions of the infrared spectrum were found useful in these determinations; the region from 1500 cm^{-1} to 1600 cm^{-1} and the portion of the "fingerprint region" from 1500 cm^{-1} to 600 cm^{-1}. The carbon-nitrogen double bond stretching absorption is usually placed at about 1630 cm^{-1} in various azomethine compounds.[12] This bond was found to absorb at 1628 cm^{-1} in benzylidineaniline, shifting to 1614 cm^{-1} in p-xylylidinedianil, 1615 cm in N,N'-bisbenzylidine-p-phenylenediamine, and 1612 cm^{-1} in the yellow solution polymer, poly(p-xylylidine-p-phenylenediamine) (DA-29-94). The corresponding high molecular weight black para polymer showed a broad absorption at 1597 cm^{-1} assigned to the carbon-nitrogen double bond.

In the meta monomer, N,N'-bisbenzylidine-m-phenylenediamine, the carbon-nitrogen double bond absorption occurs at 1623 cm^{-1}, shifting slightly in the yellow solution polymer poly(p-xylylidine-m-phenylenediamine) (DA-29-276) to 1620 cm^{-1} and finally to 1595 cm^{-1} in the black meta melt polymer (DA-42-14).

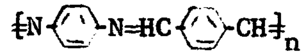
In the fingerprint region, the para black melt polymer (DA-42-12) shows two bands corresponding to 1,4 para benzene substitution at 1006 cm^{-1} (small) and 812 cm^{-1}. Monosubstituted benzene absorption, attributed to end groups and incorporated benzylidineaniline occurs at 755 cm^{-1} and 690 cm^{-1}. The black melt meta polymer shows similar bands for 1,4 para benzene substitution at 1006 cm^{-1} (small) and 825 cm^{-1} with bands attributed to monosubstitution benzene absorption at 750 cm^{-1} and 695 cm^{-1}. The bands observed in the fingerprint region of the melt Schiff base polymers corresponded closely to those observed in the spectra of the 1,4 polyphenyls[13] and the polystilbenes.[14]

Thermogravimetric analysis studies demonstrated that black, conjugated and pseudoconjugated Schiff base polymers possess high thermal stabilities. In order to ascertain the effects of high temperatures on polymer structure and to gain insights into any changes in structure which might occur, the infrared spectra of the black conjugated polymer poly(p-xylylidine-p-phenylenediamine) were examined after heating at various temperatures. This procedure involved heating polymer samples in the 950 Thermogravimetric Analyzer in nitrogen, at a heating rate of fifteen degrees per minute, and a gas flow rate of one (1) standard liter per minute. The infrared spectra of samples heated to 600, 700, 800, and 1000°C were taken using the potassium bromide discs technique. The spectra obtained after heating to 600°C and 700°C are shown in Appendix Nos. 17 and 18. Examination of these spectra in contrast with the spectrum obtained from the original polymer polymerized to 400°C showed that the bonds generally broadened and decreased in intensity as the temperature was increased. After heating to 800°C, the peaks are indistinguishable from background noise. The polymer shows no shift in the position of the carbon-nitrogen double bond absorption up to 700°C. Substantial differences, however, occur in the fingerprint region of the spectrum. As the polymer was heated from 400-700°C, the bands at 690 cm^{-1} and 1006 cm^{-1} decreased in intensity, while the band at 750 cm^{-1} increased in intensity. The band at 815 cm^{-1} remains about the same intensity, and a new peak appears at 875 cm^{-1} in the spectra taken after heating to 600°C and 700°C.

From the changes in intensity of certain bands in the spectra, and from the loss and the appearance of other bands, it appears that some structural changes in addition to further chain-end condensation occur as the polymer is heated to higher temperatures. The decrease in the 690 cm^{-1} band assigned to mono benzene substitution may be interpreted as the loss end groups due to continuing chain coupling in the solid state and to the loss of incorporated benzylidineaniline. The band at 750 cm^{-1} which had been assigned to mono-benzene substitution increases. This band has been assigned to sources other than mono-benzene substitution. Bands in this region have also been observed for substituted benzanthrenes and other polynuclear compounds having 1,2,4 benzene substitution, and for aromatic compounds having ortho 1,2 benzene substitution.[15] The band assigned to para-1,4-benzene substitution at 815 cm^{-1} remains essentially constant. The new band appearing at 875 cm^{-1} is also assigned to 1,2,4-benzene substitution or to 1,2,3,4-benzene substitution and is generally ascribed to polynuclear type compounds.[16]

It follows from these studies, that the black melt Schiff polymers undergo further condensation and chain propagation at high temperatures and that these polymers retain their Schiff base structure as written, for example, , up to about 600°C beyond which other processes begin to occur. Since spectra which are uninterpretable are obtained after heating to 800°C or higher, it is probable that not only has the molecular weight increased but that some other processes have also occurred and that the Schiff base structure has been somewhat altered.

B. Mass Spectral Analyses.

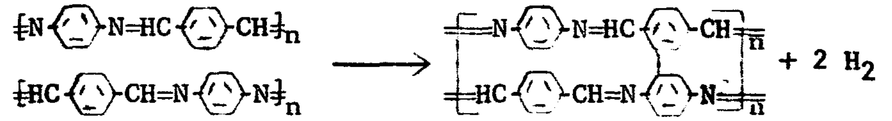
Since the infrared spectra of the polymers heated to temperatures of about 800°C indicated that changes in the structure of the black melt polymer,  (DA-42-13), might be occurring, it was desirable to obtain more information about the fate of the polymers during heating at these high temperatures. Identification of the products of a reaction often gives insight into the reaction itself. Thus, it was decided to perform a qualitative mass spectral study on the product gases formed during heating at high temperatures.

The procedure consisted of degassing two samples of the black polymer, poly(p-xylylidine-p-phenylenediamine) (DA-42-13), to 10^{-6} torr. and then heating one at 600°C and the other at 700°C for one hour. After heating, the tubes were connected directly to the mass spectrometer for analysis. Both spectra were identical and thus only the spectrum obtained after heating at 600°C is shown in Appendix No. 19.

Analysis of these spectra shows that the gas produced by this post-heating is a mixture of products. It was, however, possible to identify the major gaseous products of the reaction. The fragmentation pattern of the gases, together with major peaks located at M/e 78, 92, and 93, correspond closely to reference spectra for benzene, toluene, and aniline respectively.[17] These products may result from end group fragmentation in the polymers or from fragmentation of by-product benzylidineaniline during pyrolysis. In addition, a small amount of a yellow oil, which collected in the cooler portions of the ignition-mass spectral tubes, was examined and determined by infrared spectroscopy to be primarily benzylidineaniline. Benzylidine-aniline itself is not volatile enough to be observed in the mass spectrum.

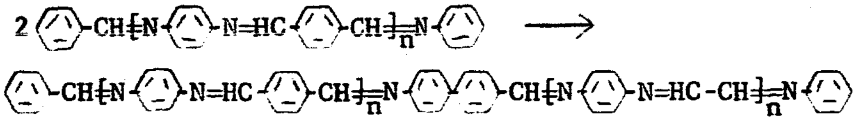
The presence of hydrogen in the spectrum is indicated by a peak at M/e 2. Since the intensity of the peaks in a mass spectrum corresponds to the relative molar concentrations of the substances present, hydrogen is the most abundant product present.

The presence of hydrogen in the mass spectrum led to a consideration of the processes which can occur in the Schiff base polymer which can give rise to this gas. Schiff base polymers may crosslink at high temperature with the elimination of hydrogen to give network polymers, as for example:



(eq. 1)

At high temperatures, chain ends may couple with the elimination of hydrogen and the formation of a diphenyl group thus increasing the molecular weight, for example:



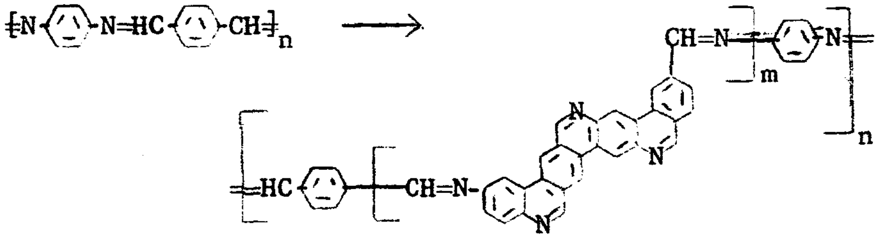
(eq. 2)

The ability of aromatic Schiff base compounds to undergo intermolecular cyclization by photolysis has been shown by Badger and his coworkers.[18]

Pyl[19] in 1927, demonstrated that the cyclization of benzylidineaniline can take place at 800°C in an iron tube in the following manner:

(eq. 3)

If a similar reaction also occurs in Schiff base polymers, a ladder polymer will be formed composed of polynuclear segmers as in equation 4



(eq. 4)

As the temperature is increased, greater portions of the polymer can condense to a ladder-type structure with the overall result that this polymer would become more thermally stable. Bruck[20] has observed this type of intermolecular rearrangement during the vacuum pyrolysis of aromatic polypyromilletimides.

Further evidence in support of intermolecular cyclization is given by the bands appearing at 875 cm^{-1} and 750 cm^{-1} in the infrared which appears after postheating and are generally attributed to highly substituted polynuclear-type compounds.

C. Calorimetric Studies.

1. Cell Constant.

Calorimetric studies were carried out in a du Pont Calorimeter Cell in conjunction with a du Pont 900 Differential Thermal Analyzer. The cell was calibrated from the known heats of fusion for indium, tin, zinc, and aluminum. Platinum liners were used, and the procedure outlined in the du Pont Manual for the Calorimetry Cell was followed. The calibration coefficients were calculated from the following equation:

$$E = \frac{(\triangle H)(m)(a)}{(A)(\triangle T_S)(T_S)}, \qquad \text{(eq. 5)}$$

where

E = the calibration coefficient in mcal/°C min.

$\triangle H$ = the heat of fusion of the metal in mcal/mg.

m = the sample mass in mg.

a = the heating rate in °C/min.

A = the peak area in square inches

$\triangle T_s$ = the Y axis sensitivity in °C/in.

T_S = the X axis sensitivity in °C/in.

The peak areas were obtained by using a polar planimeter. The calculated values for E were plotted against the transition temperatures to give the calibration curve. The experimental curve was very similar to the sample curve illustrated in the calorimetry Manual. Silver caps were used in the cell for temperatures above 350°C to reduce heat loss by radiation.

2. Behavior of Polymer DA-42-13.

Poly(p-xylylidene-p-phenylenediamine) (DA-42-13) was used as a representative polymer for the calorimetric studies. Platinum libers and silver caps were used in the runs, and the heating rate was 15°C/min. The Y axis sensitivity was 1.0°C/inc. Three tests were made on each sample, the first two in nitrogen and the third in air; all at one standard liter per minute. The conditions were the same, therefore, as those used in the thermogravimetric studies, on the same polymer. The calorimetry measurements cover the temperature range of ambient to 700°C.

a. In Nitrogen.

The black polymer (DA-42-13) (no postheating), ground 15 seconds, was used. The first test in nitrogen (Appendix No. 20, curve 1) shows a relatively small and very broad exotherm between 150 and 520°C. This appears to be a composite of two peaks, the first beginning at 150°C and the second at about 250°C. The second test (Appendix No. 20, curve 2) shows an even smaller exotherm between 370 and 560°C.

b. In Air.

The third test, in air (Appendix No. 20, curve 3) shows a very large and broad exotherm from 330 to 700°C. These results compare favorably with the thermogravimetric data (TGA) obtained on the same polymer under the same conditions. Four features, in particular, should be noted:

1) the exotherm in the nitrogen atmosphere is much smaller than that in the air atmosphere;
2) the exotherms are all very broad, suggesting a relatively slow degradative process rather than a phase change;
3) the peak of the exotherms in the calorimetry curves correspond quite well to the initial weight losses under the same conditions in the thermogravimetric curves;
4) the exotherms in the calorimetry curves begin at temperatures somewhat lower than the temperatures which show significant weight loss for the same polymer in the

thermogravimetric curves.

The third and fourth features are expecially evident in the third test performed in an air atmosphere. The third feature may possibly be due to an ablative effect. If the decomposition products are gases, it is expected that they would carry away a substantial amount of heat when they escape from the system. This possible ablative effect and the loss of material make the calculation of an accurate ΔH very difficult. The calculation is complicated further in the air atmosphere run by the fact that the curve does not return to the base line by 700°C, which is the maximum temperature for the calorimeter cell. However, heats of reaction were calculated from the curves for comparative purposes, and are reported in Table 5. The area of the curve for the air atmosphere test was obtained by doubling the area of the first half of the curve. The limitations and problems involved should be kept in mind when evaluating the relative heats of reaction. No corrections were made for weight losses. The calculated values probably represent the correct order of magnitude for the lower limit of the heats of reaction in each case. The very large value of ΔH for the air-atmosphere test should especially be noted.

3. Behavior of Polymer Postheated to 1000°C.

A sample of the same polymer which had been postheated to 1000°C (DA-42-13), H-1000) was run in the calorimeter cell under nitrogen and air (Appendix No. 21), at a flow rate of one standard liter per minute and a heating rate of 15°C per minute. Again, a very broad and relatively small exotherm is evident in the nitrogen run, and a broad and very large exotherm is evident in the air run. The peak temperatures and heats of reaction are recorded in Table 5. The peak temperatures are approximately 25°C higher for this sample than for the untreated polymer. Otherwise, the curves are very similar.

Table 5

Calorimetric Data on Poly Schiff Bases and Graphite

Polymer	Atmosphere	Approx. Temp. of Initial Weight Loss °C	Calorimetry Peak Temp. °C	Initial Sample Weight, mg.	Calculated Heat of Reaction cal./g.
DA-42-13 15°C/min.	N_2	400	420	4.5	170- 180
	N_2	---	500		75- 85
	air	500	550		2700-3000
DA-42-13-H1000 15°C/min.	N_2	---		1.7	400- 450
	air	---	575		4900-5500
DA-42-13 5°C/min.	air	420	400 535	3.2	3000-3500
Pyrolytic Graphite 15°C/min.	air	650	680	4.7	520- 550
DA-29-94 Yellow Polymer 5°C/min.	air	410	400 525	2.7 (est. 1.4)	1700-2000 4900-5500

In order to study the effect of heating rate on the curve, a sample of DA-42-13 was run at 5°C/min. in air (Appendix No. 22). The resulting curve appears to be a composite of two exotherms, the first with a maximum around 400°C, and the second with a maximum at 535°C. The calculated heat of reaction in Table 5, is for the complete curve. In this case, the curve returns to a base line by 700°C.

Another observation should be mentioned in connection with this test. The initial weight of sample was 3.2 mg. The amount of sample remaining after the run to 700°C was 2.1 mg. Under the same conditions of heating rate and air flow, the thermogravimetric curve (Appendix No. 3) shows that the polymer is completely decomposed by 700°C. This discrepancy shows that care must be taken in comparing the thermogravimetric results with the calorimetric results. The difference is probably due to the fact that, in the calorimeter cell, the sample is placed in a platinum liner inside a small cup which is then covered by a cap. In addition, a cover is placed over the cell compartment. As a result, the air flow over the sample is undoubtedly much less in the calorimeter cell than in the thermogravimetric boat, where the air flows directly over the sample.

4. Behavior of Pyrolytic Graphite.

A sample of pyrolytic graphite was run in the calorimeter under nitrogen and air up to 700°C (Appendix No. 23) for comparison with the polymer DA-42-13. There is no evidence of an exotherm or endotherm in the nitrogen run. The run in air shows a broad and relatively weak exotherm beginning around 400°C and reaching a maximum at 680°C. The heat of reaction is reported in Table 5. The area of the curve was obtained by doubling the area of the first half. It should be noted that the heat of reaction obtained for the graphite in air is much less than that obtained for the polymer, DA-42-13, and that the maximum in the graphite curve is over 100°C higher than that in the polymer curve.

a. DA-29-94 - Yellow Polymer.

A calorimetric test was made on a sample of the yellow polymer, DA-29-94 (Appendix No. 24) for comparison with the black polymer. The test was made in an air atmosphere and at 5°C/min. The curve shows two exotherms, the first with a maximum at 400°C, and the second with a maximum at 525°C. It should be noted that the black polymer sample (DA-42-13) under the same conditions gave a very similar calorimetric curve, except that the 400°C peak was much weaker. Calculated heats of reaction for the two exotherms are recorded in Table 5. The areas of the curves were obtained by doubling the area of the first half of the first peak and the last half of the second peak, respectively. The thermogravimetric curve for the same polymer under the same conditions of air flow and heating rate showed a large weight loss between 410 and 425°C which probably corresponds to the first exotherm of the calorimetry curve. For the calculation of $\triangle H$ from the second exotherm, it was assumed that approximately 50% of the initial weight of sample had been lost, and therefore 1.4 mg. was used as the mass of the polymer in the second calculation.

Even though the calculated heats of reaction in this study can be considered to reflect only the relative order of magnitude of the true heats of reaction, it seems evident that much more information can be obtained from the calorimetric studies than from simple differential thermal analysis. The evidence, however, indicates that, when the Schiff base polymers are heated to 1000°C, they have not been converted to graphitic polymers.

IV. Stability of Schiff Base Polymers to Ionizing Radiation.

When a polymer is subjected to ionizing radiation, either a crosslinked or degraded polymer is obtained.[21-26] The amount of crosslinking and degradation which occurs in a polymer has been shown to be dependent on a number factors:

1) the monomer and polymer structures;
2) the effect of oxygen;
3) the protection of aryl groups;
4) the linkages present in the polymer;
5) the molecular weight.

Hence, the requirements for radiation stability parallels those for thermal stability, and polymers which have been shown to possess thermal stability are also generally radiation resistant. For example, the thermally stable polyimidazopyrrolones possess good radiation stability as well as thermal stability.[27] Polymers possessing aromatic structures in the backbone appear to be especially resistant to radiation. Thus, it has been shown that aliphatic saturated polyesters possess poorer radiation resistance than polyesters containing aromatic moieties such as polyethyleneterephthalate.[28] The effect of these aromatic moieties is to act as energy sinks which are able to delocalize either thermal or radiolytic energies and hence, to protect the polymer structure from gross degradation.

From these considerations, the high molecular weight, conjugated Schiff base polymers prepared in this research are also expected to possess very high radiation resistance. A Schiff base polymer which would be expected to possess high radiation resistance is the completely conjugated polymer, poly(p-xylylidene-phenylenediamine), . This polymer has been shown to possess very high thermal stability of the order of 1176°C in nitrogen and 600°C in air. Due to the nature of its conjugation, this polymer would be expected similarly to dissipate and delocalize radiolytic energies.

Thus it was decided to evaluate the radiation resistance of the Schiff base polymers by comparing the thermal stability of the polymers before and after irradiation. The polymer DA-42-13, poly(p-xylylidine-p-phenylenediamine), as prepared at 400°C and also postheated to 600°C was taken to be representative of Schiff base polymers in general and was investigated in this study.

This study was divided into three parts:

1) polymers irradiated in vacuo;
2) polymers irradiated after sealing in air;
3) polymers exposed to air during irradiation.

The polymer samples were irradiated by exposure to the Cobalt source at the NASA-Langley Research Center, Hampton, Virginia at a dose rate of 1.2

megareps per hour at an ambient temperature of 47°C.

The general procedure consisted in irradiating polymer samples with a dosage of 200 megarads and then subjecting them to thermogravimetric analysis in nitrogen and in air and comparing the resulting thermograms with those of non-irradiated samples already reported in the previous report.[1] The experimental parameters for these analyses were those used in the earlier studies,[1] the following:

1) a flow rate of one (1) standard liter per minute;
2) a heating rate of 15°C per minute;
3) a grinding time for non-powder samples of fifteen seconds in a stainless steel grinding capsule.

A. Polymers Irradiated at Reduced Pressure.

The powdered samples (500 pieces/10 mg.) were degassed at 10^{-6} torr. for one hour prior to irradiation. The thermograms obtained in nitrogen and in air for polymer DA-42-13 condensed to 400°C and for the same polymer, DA-42-13-H600 postheated to 600°C are shown in Appendix Nos. 25 and 26. Comparisons of these thermograms with the corresponding thermograms of non-irradiated samples shows no detectable difference in thermal stabilities of polymers before and after irradiation. The pressure in the sample vials, after irradiation, was still very low, indicating that no appreciable amounts of gas were generated during the irradiation process.

B. Polymers Irradiated After Sealing in an Air Atmosphere.

That oxygen contributes to the overall effect of radiation damage is well known. It was, therefore, decided to determine the effect of this parameter on the radiation stability of polymers irradiated in this atmosphere.

Specimens for irradiation were prepared by sealing 40 mg. of powdered polymer in a glass tube containing about 5 cc. of air at atmospheric pressure. Four thermograms (Appendix Nos. 27 and 28) were recorded of polymers DA-42-13 and DA-43-13-H600 in nitrogen and in air. A comparison of these thermograms with those obtained from previous non-irradiated samples shows no detectable diminution of the thermal stability due to irradiation.

C. Polymers Irradiated While Exposed to Air During Irradiation.

Since there may be a difference between samples sealed in air and samples left open to air during irradiation, it was decided to investigate this parameter. The samples in this study were placed in screw cap vials open during irradiation. The thermograms of these polymers are shown in Appendix Nos. 29 and 30. In these cases, as in the others, little or no difference can be distinguished in the thermograms before and after irradiation.

These irradiation studies confirm the prior assumption that Schiff base polymers possessing a high degree of thermal stability would also possess high radiation stabilities.

V. Summary and Conclusions.

1. The thermal stability of poly(p-xylylidene-p-phenylenediamine) is the same in nitrogen and in helium.
2. Poly(p-xylylidene-p-phenylenediamine) prepared at 400°C shows a stability in 100% oxygen of about 450°C.
3. The thermal stability values of poly(p-xylylidene-p-phenylenediamine) in a nitrogen atmosphere are unchanged over a fourfold change in gas-flow rate.
4) The thermal stability values of poly(p-xylylidene-p-phenylenediamine) in an air atmosphere are unchanged over a fourfold change in gas-flow rate.
5. Only minor changes in the heat stability values of poly(p-

xylylidene-p-phenylenediamine) are found in nitrogen or in air with changes in the heating rates in the range of 5°C to 30°C per minute.

6) The thermal stability of poly(p-xylylidene-p-phenylenediamine) appears to be higher in nitrogen and in air when a solid mass rather than a powdered sample is used.

7) The thermal stability values of the Schiff-base polymers given in a prior report[1] were determined on powdered samples containing approximately 500 pieces per 10 mg. represent the "true" and "practical" stabilities. In massive form, these values would be appreciably higher.

8) Infrared analyses confirm the Schiff base character of the polymers. Spectral regions were assigned to prominent bonds.

9) Changes in the infrared spectra become evident when the polymer is heated to temperatures of about 600°C as a result of extension due to chain-end coupling, and elimination of benzalaniline while retaining their Schiff-base structure. Other structural changes occur after heating to 700°C or higher.

10. Mass spectral analyses indicate that hydrogen is the most abundant product when the polymer is heated to 700°C or higher. Products from the fragments of benzylideneaniline are also present. The infrared spectra give evidence that some ladder-type structures may have formed in the polymer due to heating at high temperatures.

11. A comparative calorimetric study of the Schiff-base polymers and pyrolytic graphite indicate that the Schiff-base polymer is not "graphittized" when heated to 1000°C in nitrogen.

12. The thermogravimetric analysis data give no evidence of changes in the Schiff polymers when subjected to 200 megareps of cobalt 60 irradiation either in vacuo or with the samples continuously exposed to air.

VI. Future Studies.

1. Initiate studies on the direct synthesis of polymers in a one-stage melt-process from aniline, benzaldehyde and the following pairs of aromatic diamines and dialdehydes:

   1) p-phthaldehyde and p-phenylenediamine;
   2) p-phthaldehyde and m-phenylenediamine;
   3) m-phthaldehyde and m-phenylenediamine;
   4) m-phthaldehyde and p-phenylenediamine;

   which are expected to yield respectively

   a) the para-para-
   b) the para-meta-
   c) the meta-meta-
   d) the meta-para-

   xylylidinephenylenediamine polymers.

2. Evaluate and compare the polymers obtained by the above direct melt process with those prepared by the Schiff base exchange method.

3. Determine the extent of polymerization at which the fusible polymers should be isolated for post-conversion to the infusible state:

   a) Evaluate use of Lewis acids in the conversion step.

4. 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 computer programming to attempt to solve this problem.

5. Undertake appropriate physical studies involving the following solid state properties of selected polymers 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.
6. Attempt to determine molecular weight of polymers by end-group analysis using perfluoro compounds such as F_5H_6CHO and $F_5C_6NH_2$ as end groups in the bis-Schiff bases, $F_5C_6CH{=}N{-}C_6H_4N{=}HC{-}C_6H_5$, and $F_5C_6N{=}HC{-}C_6H_4{-}CH{=}N{-}C_6H_5$ from which the polymers are prepared.
7. 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.
8. Initiate study to evaluate the photoconductivity of the polymers as a function of
    a) wavelength of the incident light,
    b) temperature.

VI. Bibliography.

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

2. W.J. Smothers and Y. Chiang, Differential Thermal Analysis, Chem. Pub. Co., New York (1958).

3. S. Strella, J. App. Polym. Sci., 7, 569 (1963).

4. C.R. Doyle, J. Appl. Polym. Sci., 6, 639 (1962).

5. W.W. Wright, Soc. Chem. Ind. (London), Monograph 13, 248 (1961).

6. C. Duval, Inorganic Thermogravimetric Analysis, Chap. 1, Elsevier New York, 1963.

7. E.L. Simons, A.E. Newkirk and I. Aliferis, Anal. Chem., 29, 48 (1957).

8. W.J. Smothers and Y. Chiang, Differential Thermal Analysis, Chap. 1, Chem. Pub. Co., New York, 1958.

9. C.D. Doyle, Anal. Chem., 33, 77 (1961).

10. V.L. Bell, G.F. Pezdirtz, Am. Chem. Soc., Polymer Preprints, 6, No. 2, 742 (1965).

11. A.D. Delman, B.B Simons, A.A. Stein, R.J. Katzenstein, Am. Chem. Soc., Polymer Preprints, 7, No. 1, 77 (1961).

12. L.J. Bellamy, The Infra-Red Spectra of Complex Molecules, John Wiley and Sons, New York, 1962, p. 270.

13. C.S. Marvel and G.E. Hartzell, J. Am. Chem. Soc., 81, 488 (1959).

14. D.A. Frey, M. Hazegawa and C.S. Marvel, J. Poly. Sci., A-1, 2057 (1963).

15. L.J. Bellamy, ibid., p. 77.

16. S.F.D. Orr and H.W. Thompson, J. Chem. Soc., 218 (1950).

17. American Petroleum Institute Research Project 44, Chem. and Pet. Research Lab., Carnegie Institute of Technology, Pittsburgh, Pennsylvania, 1959.

18. G.M. Badger, C.P. Joshua and G.E. Lewis, Tetrahed. Letters, 49, 3711 (1964).

19. G. Pyl, Ber., 60, 287 (1927).

20. S.D. Bruck, Polymers (London), 6, [6], 319 (1965).

21. A. Charlesby, Nature (Letters to the Editors), 171, No. 4343, 167 (1953).

22. A.A. Miller, E.J. Lawton and J.S. Balwit, J. Poly. Sci., 14 No. 77, 503 (1954).

23. L.E. St. Pierre and H.A. Dewhurst, J. Chem. Phys., 29, [1], 241 (1958).

24. M. Dole, Paper 7 of Rep. of Symposium IV, Chemistry and Physics of Radiation Dosimetry (U.S. Chem. Center, Edgewood, Md.), September 18-20, 1950.

25. P. Alexander and A. Charlesby, Nature, 173, No. 4404, 578 (1954).

26. E.J. Lawton, A.M. Bueche and J.S. Balwit, Nature, 172, No. 4367, 76 (1953).

27. G.F. Pezdirtz and V. Bell, NASA Technical Note, NASA TND-3148 (1965).

28. G.F. D'Alelio, G.F. Pezdirtz and R. Häberli, Effect of Ionizing Radiation on a Series of Polymers, NASA Special Report, NASA Sp-58, (1964).

VIII. Acknowledgment.

The authors and the University of Notre Dame gratefully acknowledge the financial assistance which made this research possible. We express our thanks also to Dr. George Pezdirtz, NASA Langley Research Center, Hampton, Virginia for the irradiation of the polymer samples. Appreciated also is the general guidance and assistance given by Mr. Bernard Achhammer, NASA Headquarters, Washington, D. C. 20546.

Appendix No. 1

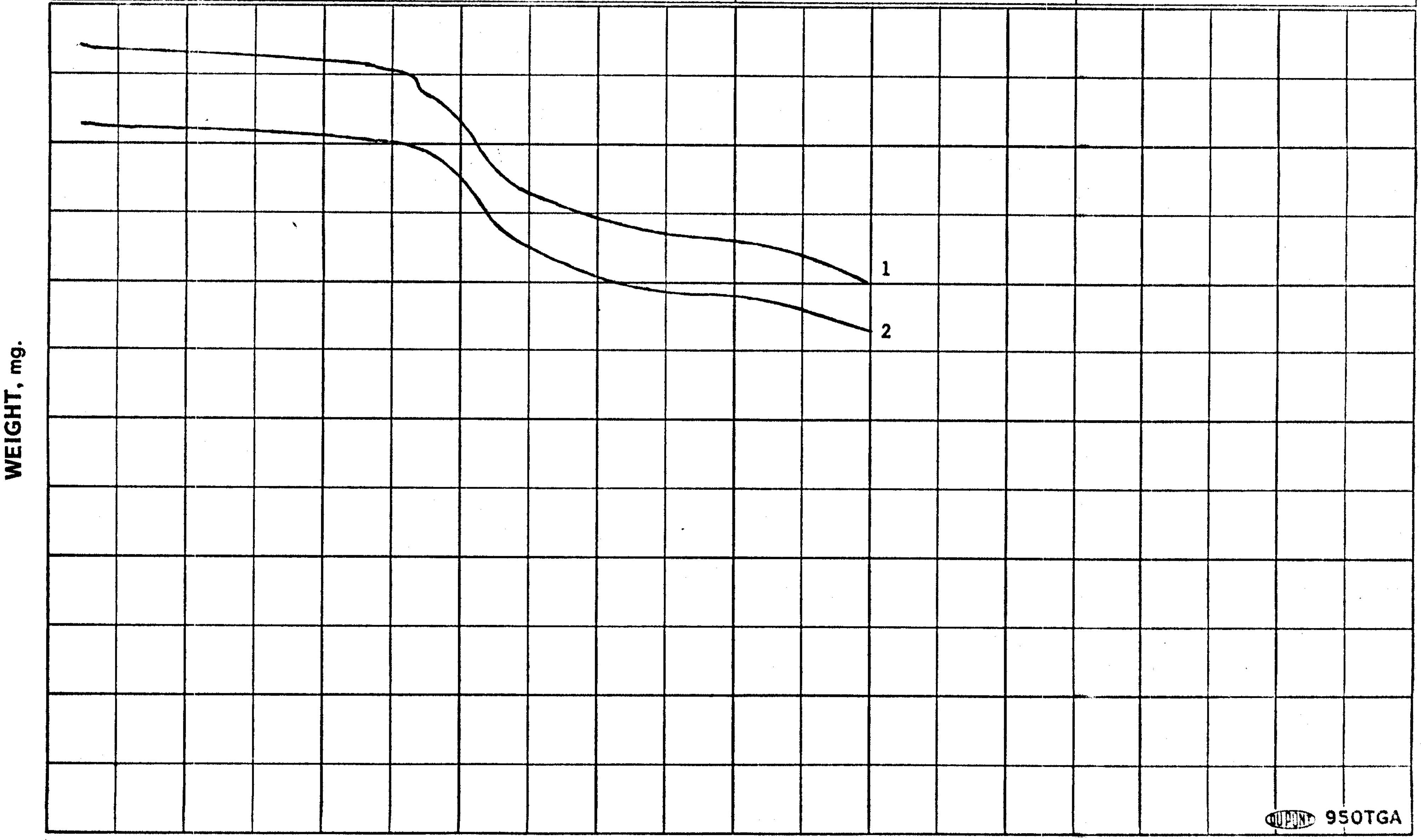
E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-42-13
$\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$
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 10-15-65
OPERATOR JVC
HEATING RATE 15 °C/min.
ATM. 1) helium; 2) nitrogen
TIME CONSTANT 2 sec.

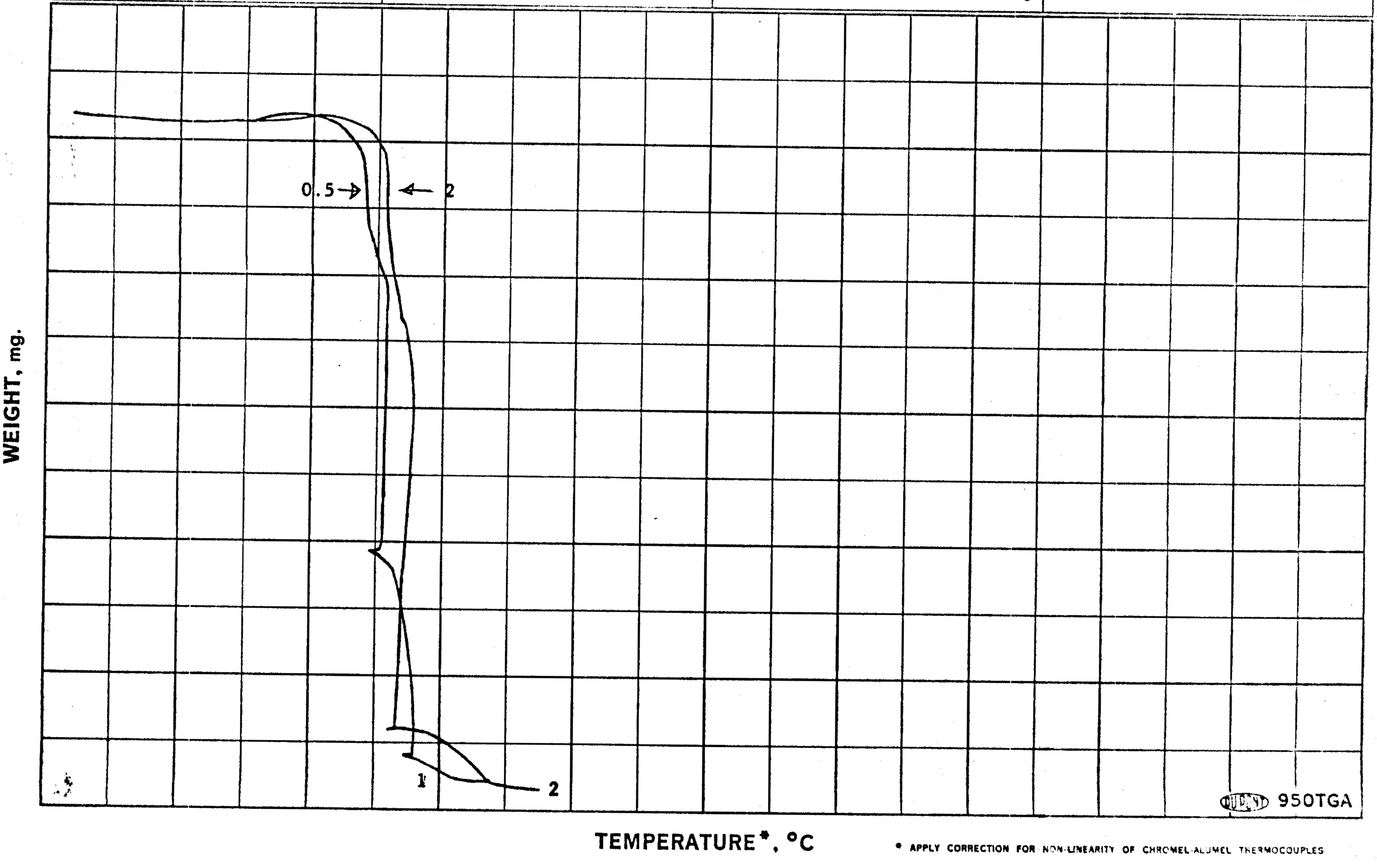


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 2

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

SAMPLE: DA-42-13 $\{\mathrm{N-C_6H_4-N=HC-C_6H_4-CH}\}_n$ 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 11-18-65 OPERATOR TD HEATING RATE 15 °C/min. ATM. O_2, 0.5 & 2 Std 1/min. TIME CONSTANT 2 sec.

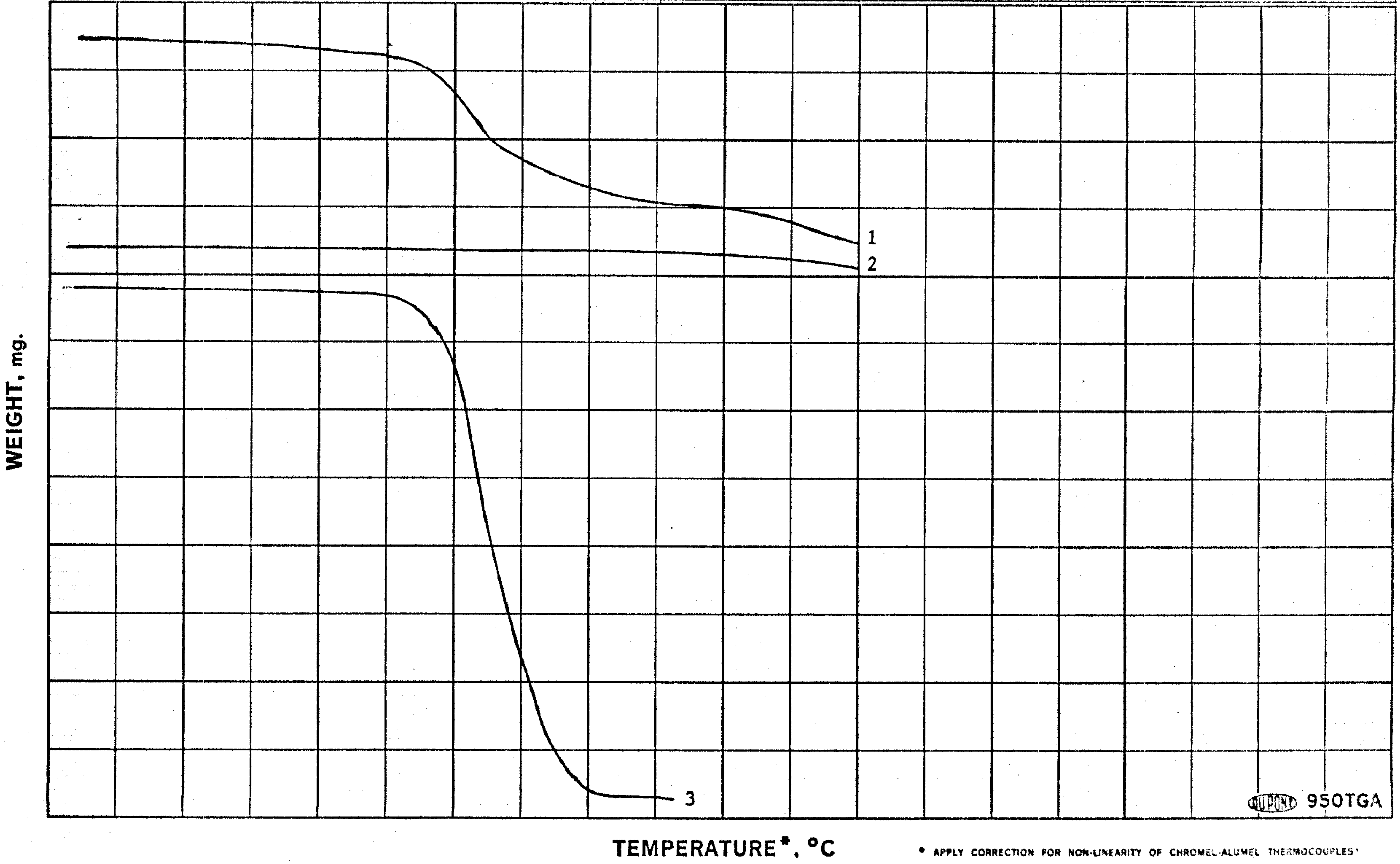


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 3

DUPONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE: DA-42-13	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.

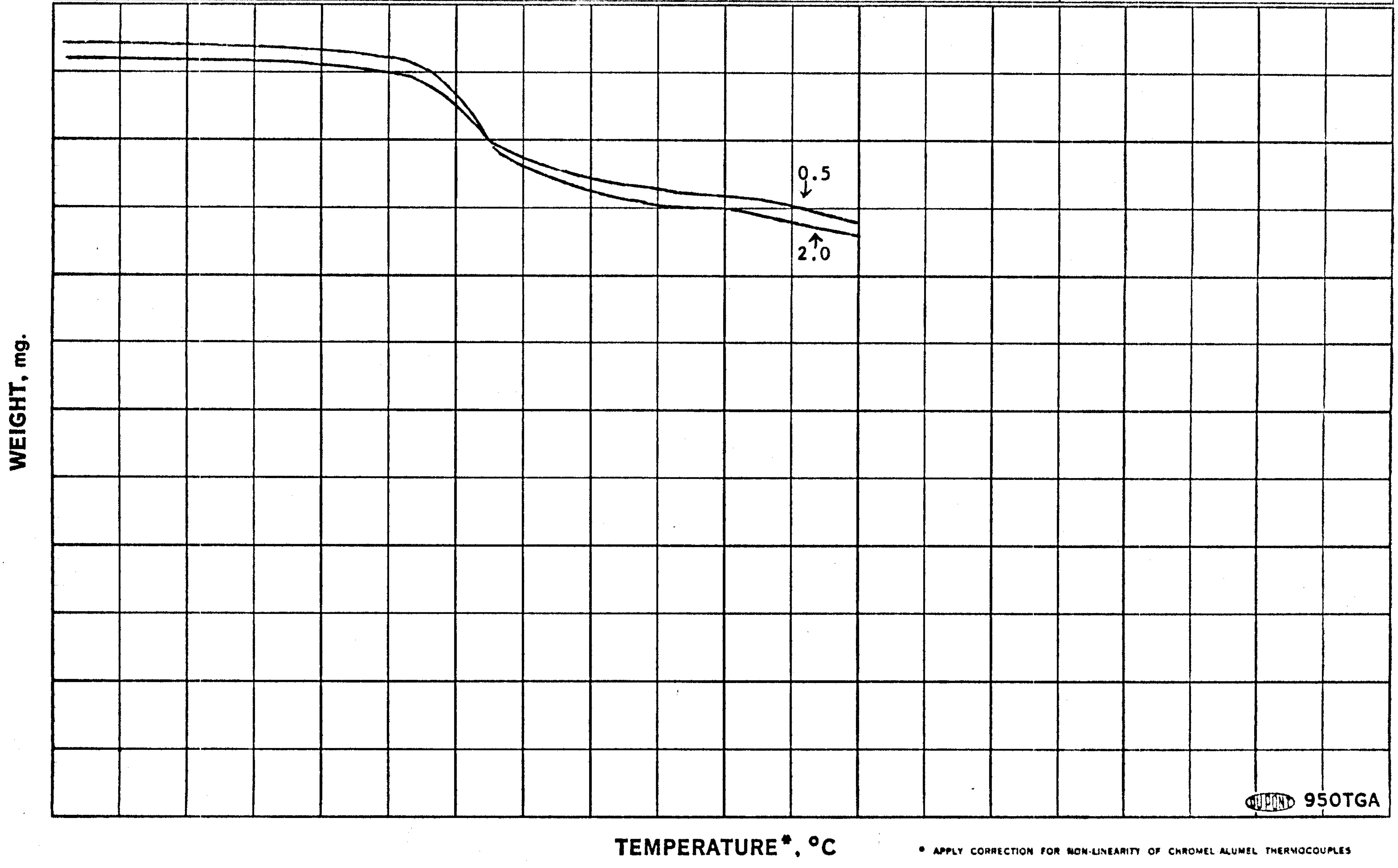


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES.

Appendix No. 4

DU PONT | INSTRUMENT PRODUCTS DIVISION

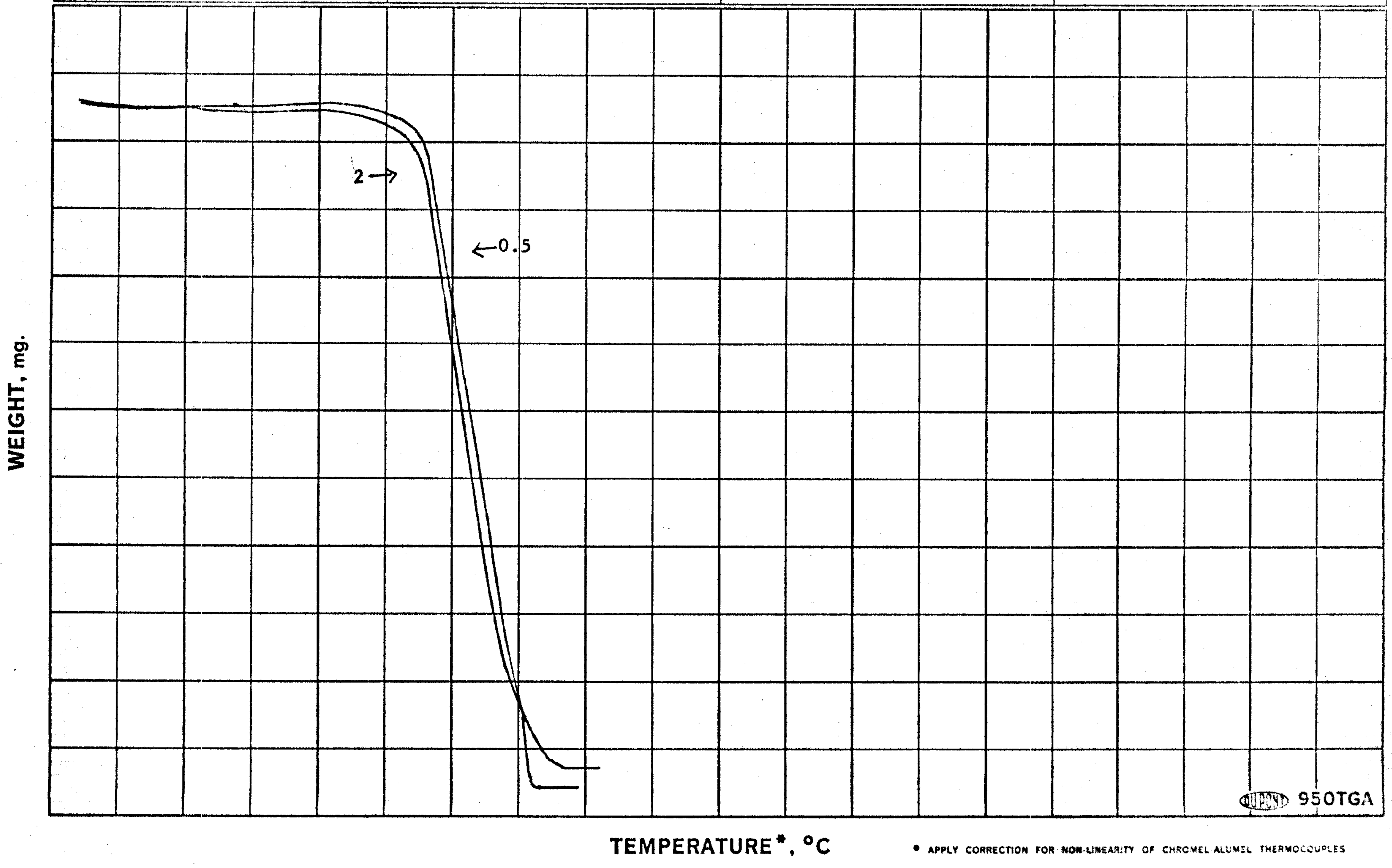
SAMPLE: DA-42-13	X-AXIS	Y-AXIS	RUN NO. ____ DATE 2-20-65
$\{N-C_6H_4-N{=}HC-C_6H_4-CH\}_n$	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch	OPERATOR JVC
	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C/min.
			ATM. N_2, 0.5 & 2 Std 1/min.
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-42-13	X-AXIS	Y-AXIS	RUN NO. ______ DATE 11-18-65
$+N-C_6H_4-N=HC-C_6H_4-CH+_n$	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch	OPERATOR TD
	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C/min.
			ATM. Air, 0.5 & 2 Std 1/min.
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

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-42-13
$\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$

SIZE ______ mg.

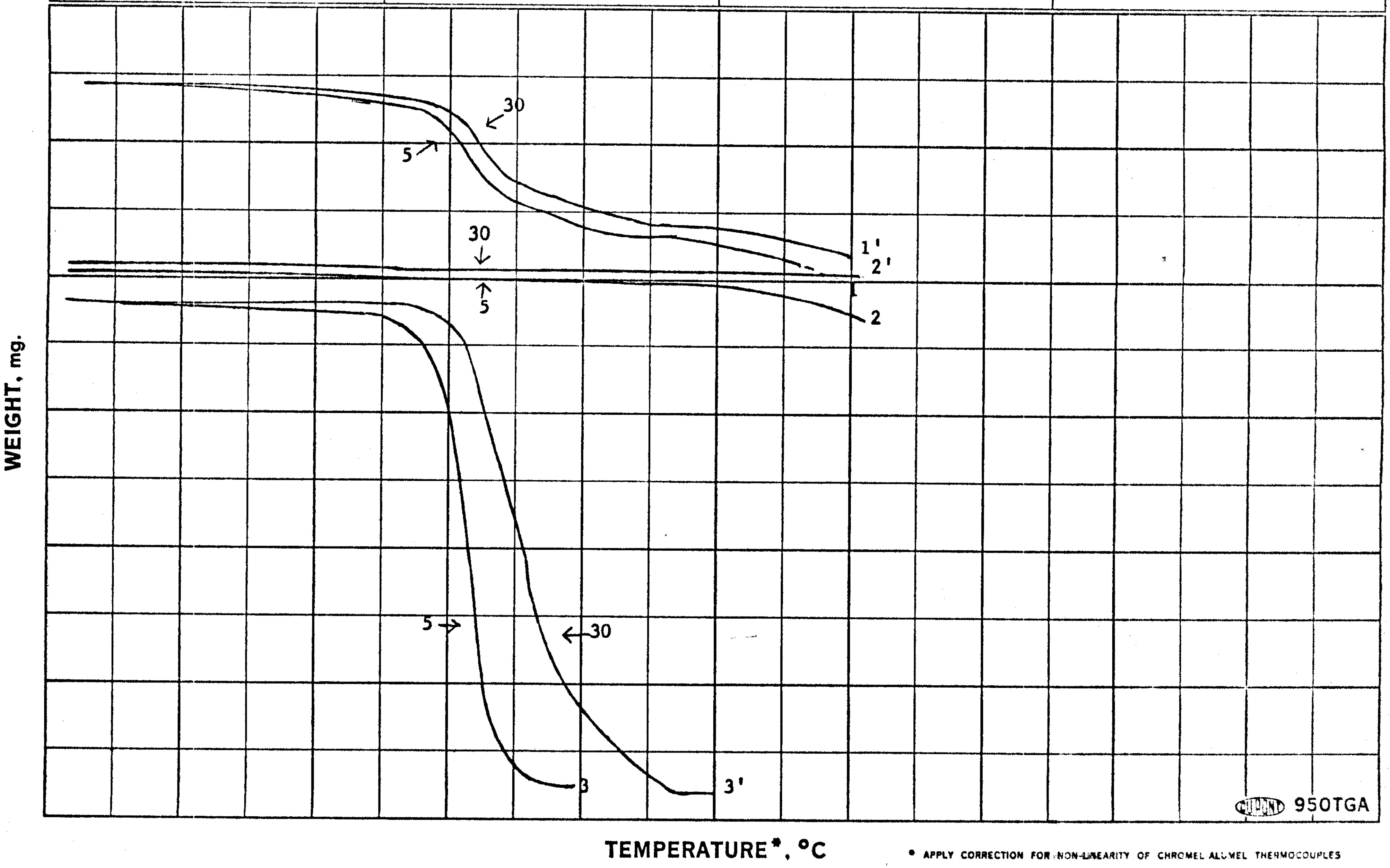
X-AXIS

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 11-16-65
OPERATOR TD
HEATING RATE 30 and 5 °C*/min.
ATM. 1) N_2; 2) N_2; 3) air
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

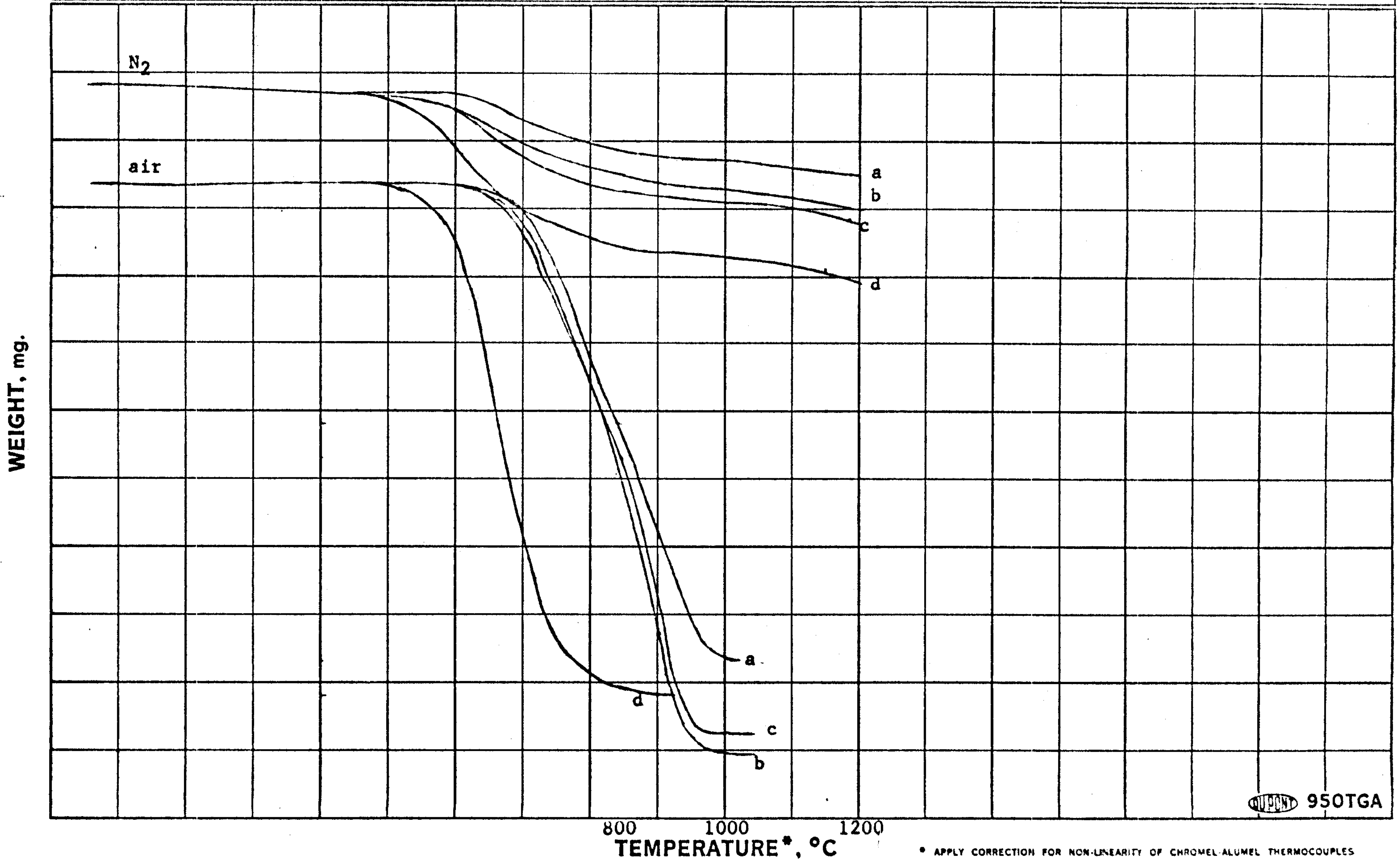
E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-42-13
1 piece - a
4 pieces - b
22 pieces - c
500 pieces - d
SIZE ____ mg.

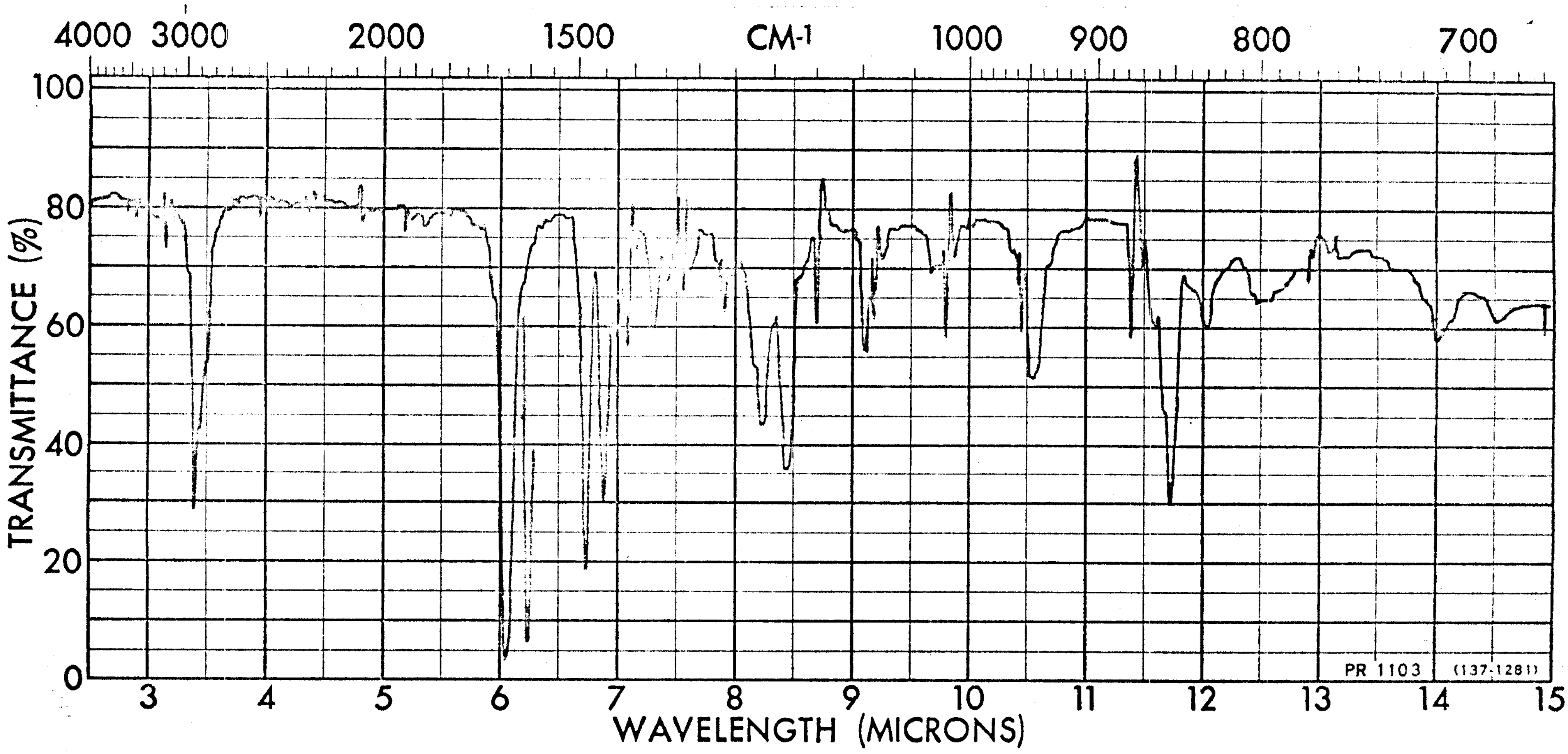
X-AXIS
TEMP. SCALE 200 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

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

RUN NO. ____ DATE 1-22-66
OPERATOR TD
HEATING RATE 15 °C/min.
ATM. N_2 & air 1 Std 1/min.
TIME CONSTANT 2 sec.

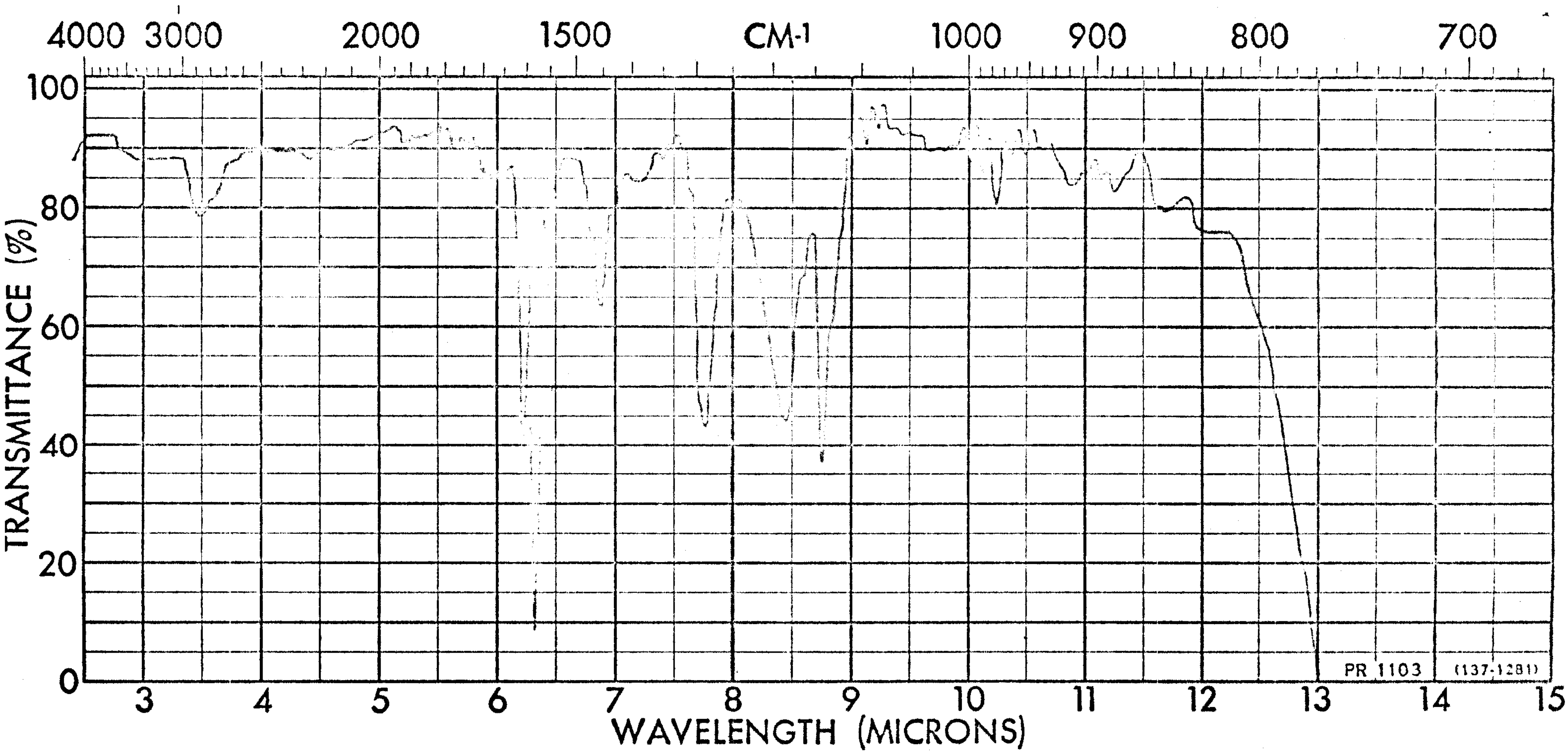


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES



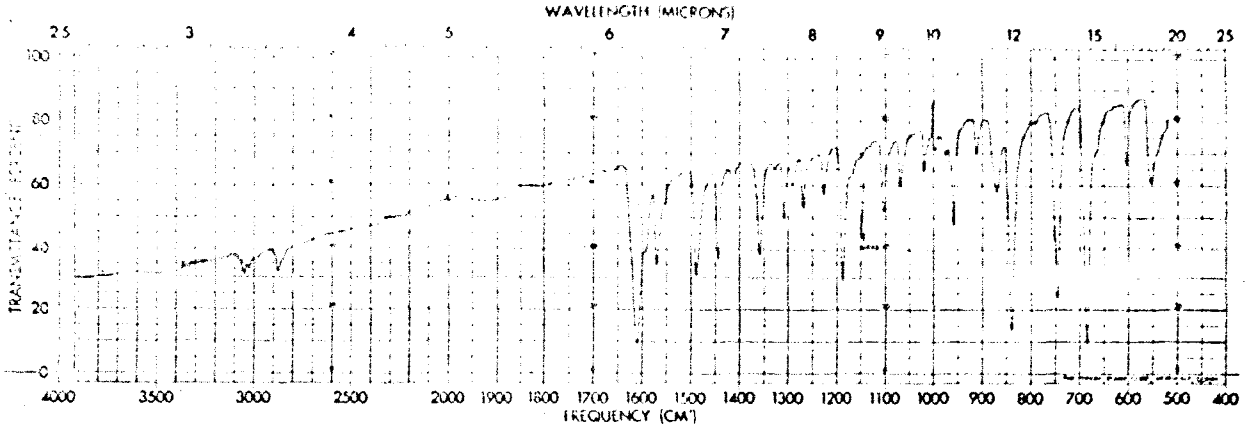
Appendix No. 8 N,N'-Bis(3-pentylidine)-p-phenylenediamine

Neat



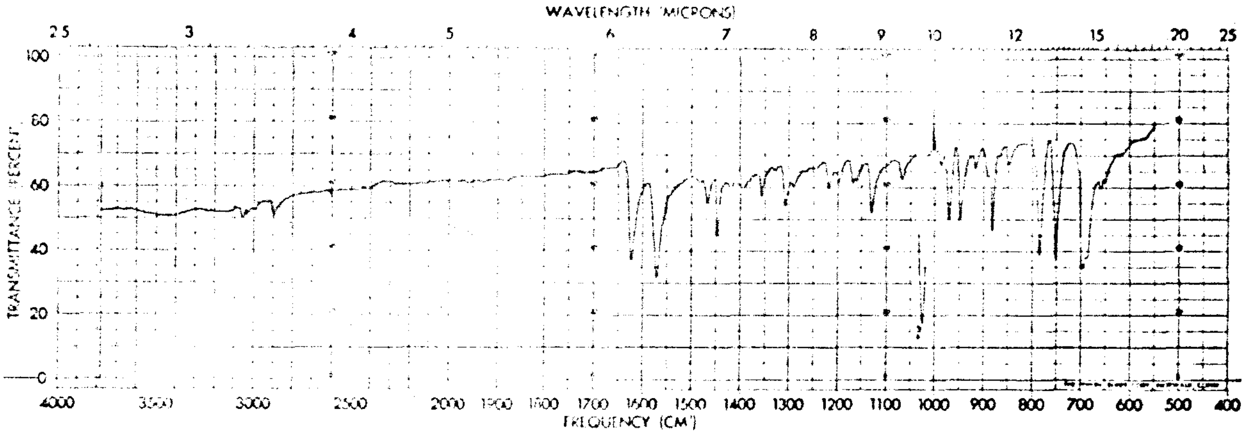
Appendix No. 9   3,7-Bis(benzylidineamino)thiaxanthene-5,5-dioxide

5% Solution in Chloroform



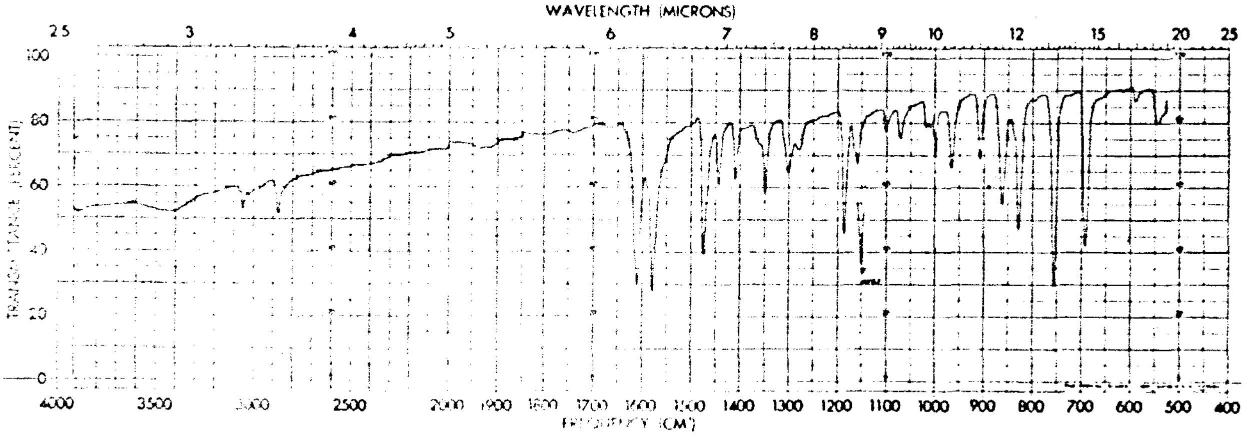
Appendix No. 10 N,N'-Bisbenzylidine-p-phenylenediamine

KBr Disc



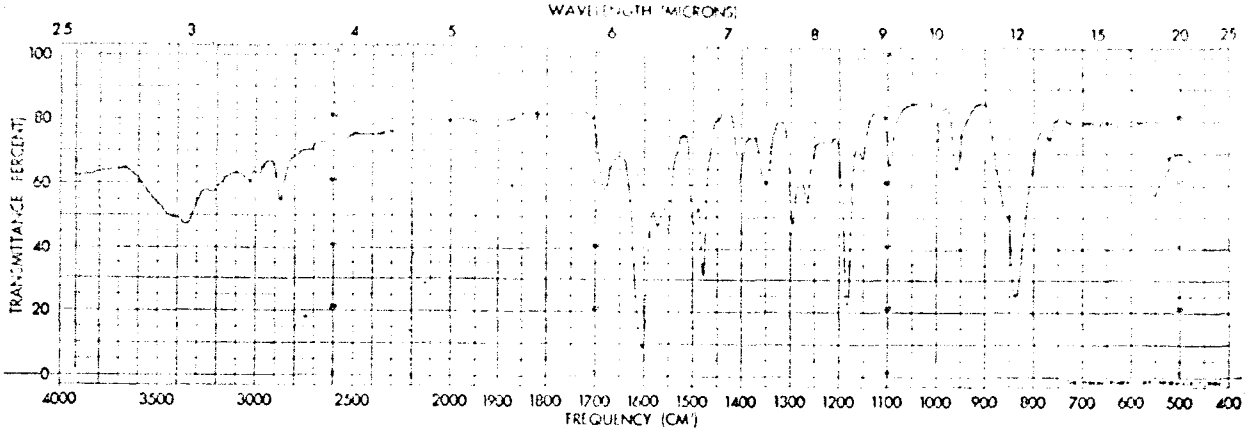
Appendix No. 11 N,N'-Bisbenzylidine-m-phenylenediamine

KBr Disc

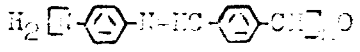


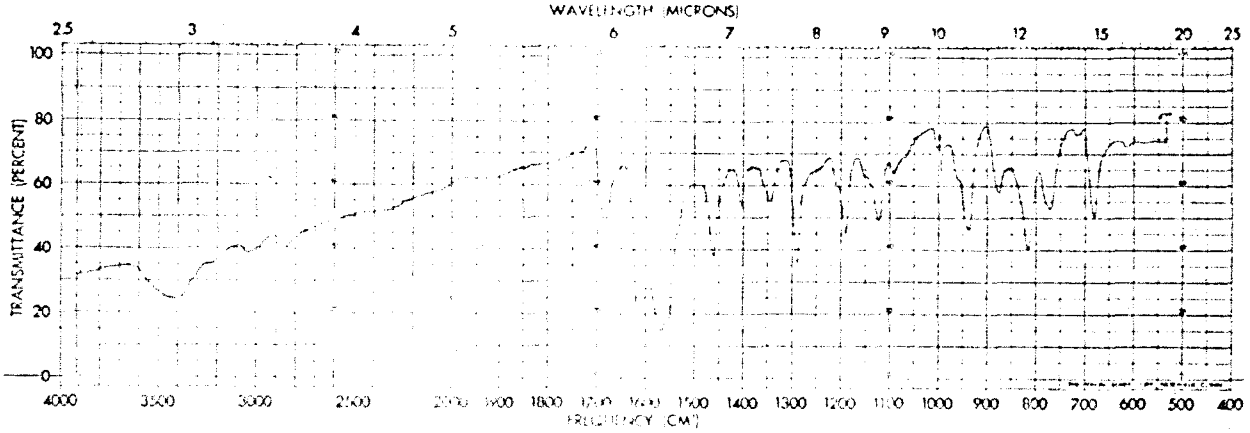
Appendix No. 12 p-Xylylidinedianil

KBr Disc

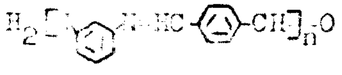


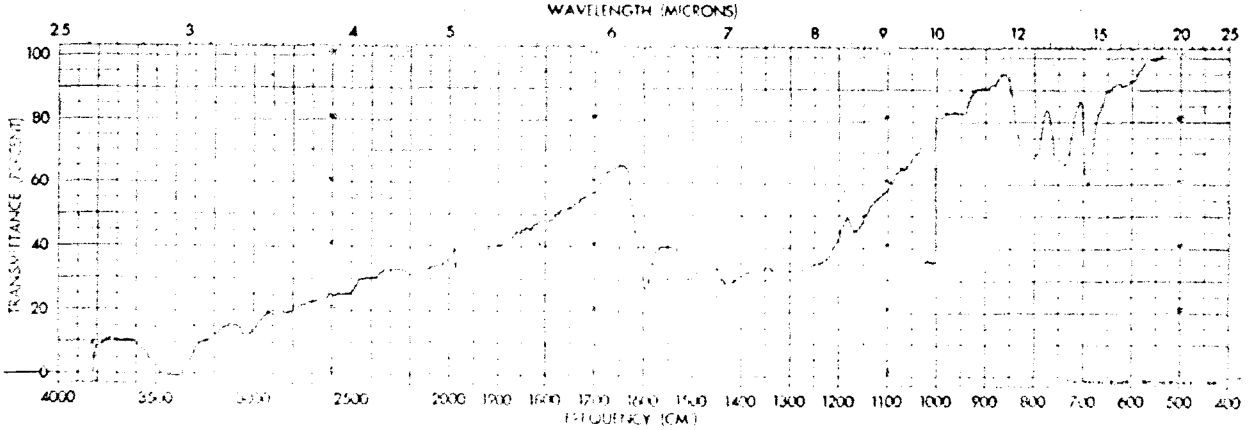
Appendix No. 13 Yellow Solution Polymer
KBr Disc



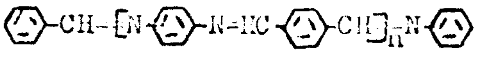


Appendix No. 14 Yellow Solution Polymer
KBr Disc

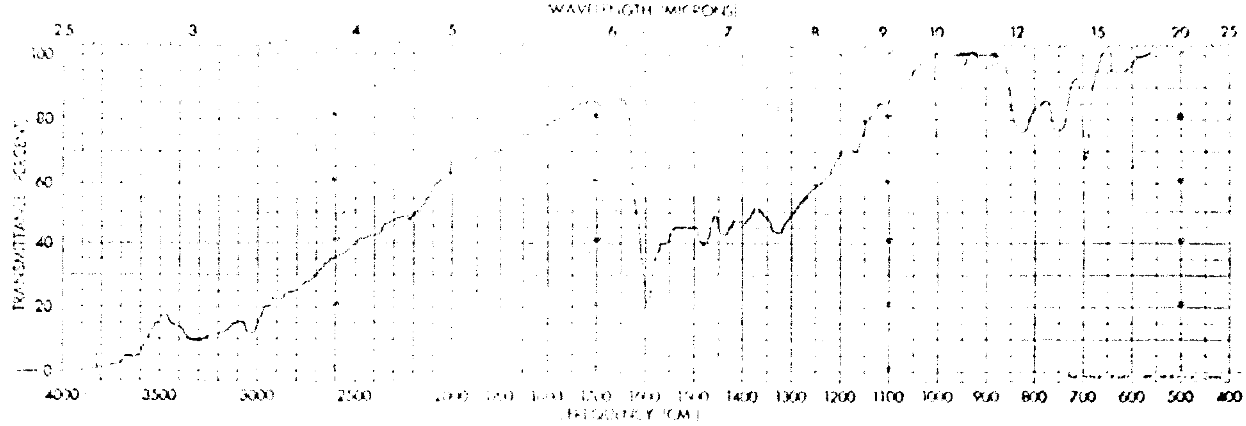




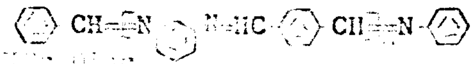
Appendix No. 15 Black Bis-Schiff Base Exchange Polymer



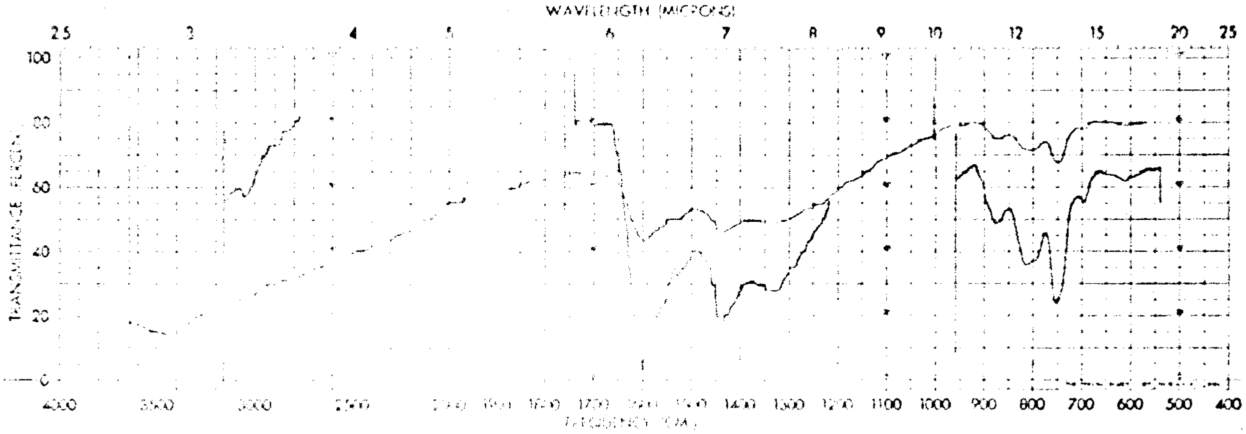
KBr Disc



Appendix No. 16 Fresh Bis-Schiff Base Exchange Polymer

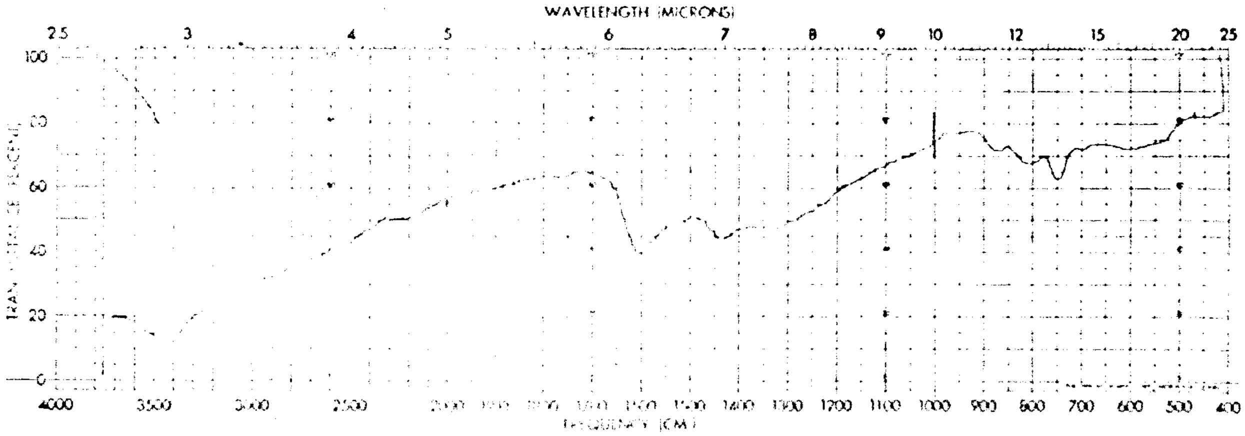


KBr Disc



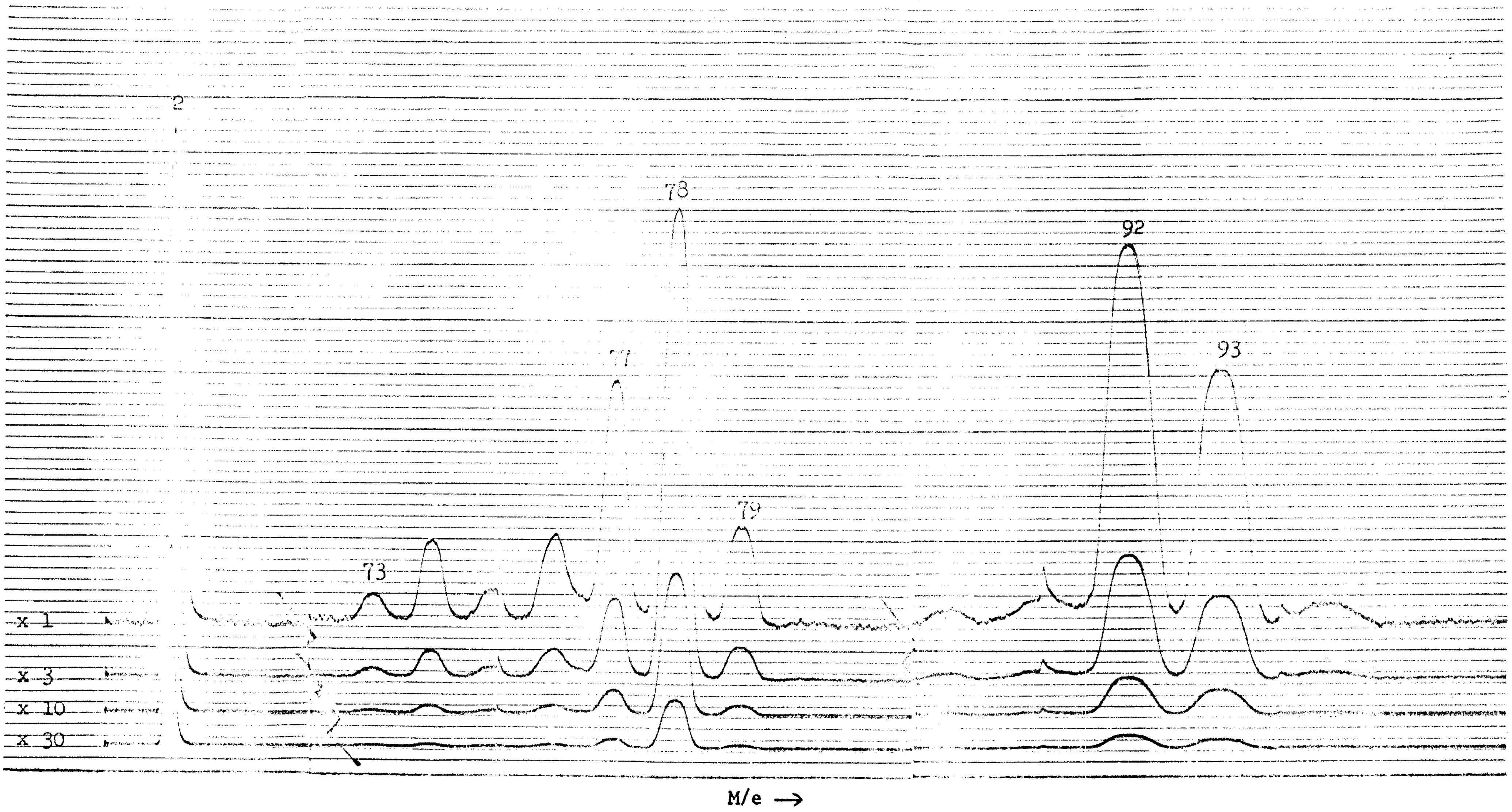
Appendix No. 17 Bis-Schiff Base Exchange Polymer Postheated to 600°C

KBr Disc

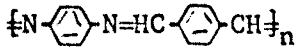


Appendix No. 18 Bis-Schiff Base Exchange Polymer Postheated to 700°C

KBr Disc



Appendix No. 19. Mass Spectrum of the Products of the Polymer

 Heated at 600°C

Appendix No. 20

SAMPLE: ______ RUN NO.: ______

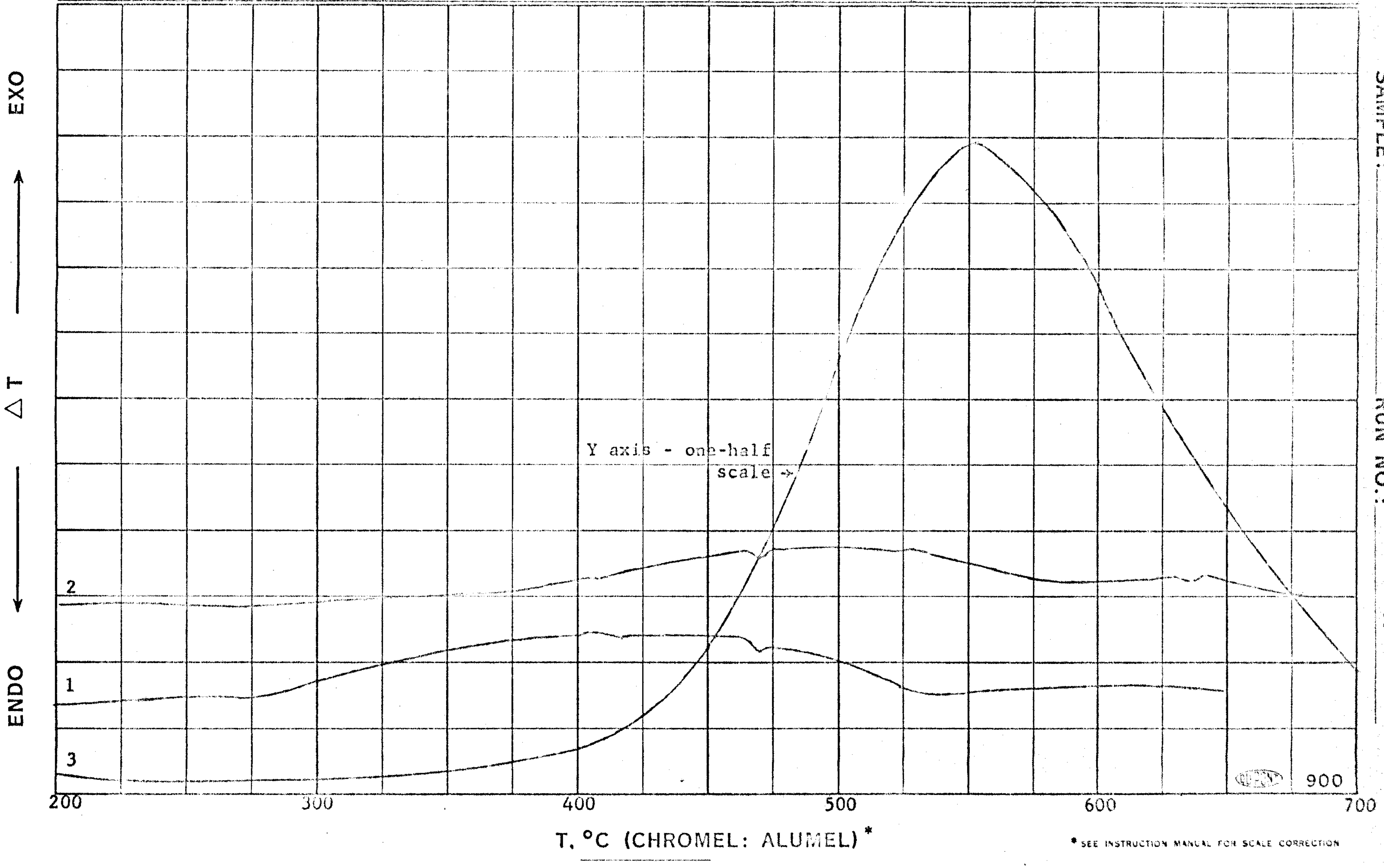
SAMPLE: DA-42-13
$[N-C_6H_4-N=HC-C_6H_4-CH]_n$
black polymer
ORIGIN:

SIZE 4.5 mg.
REF.
PROG. MODE heat
RATE 15 °C/MIN, START ______ °C

ATM. 1) N_2; 2) N_2; 3) air, 1 Std 1/mMM

	T	△T
SCALE	50 °C/IN.	1.0 °C/IN.
SHIFT	0 IN.	as req. IN.

RUN NO.
DATE 1-11-66
OPERATOR TD
BASE LINE SLOPE 0



* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

Appendix No. 21

SAMPLE: RUN NO.:

SAMPLE: DA-42-13-M1000

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

ORIGIN:

SIZE 1.7 mg.

REF.

PROG. MODE heat

RATE 15 °/m, START °C

ATM. 1) N2 2) air, 1 std l/min. MM

SCALE T 50 °C/IN. ΔT 1.0 °C/IN.

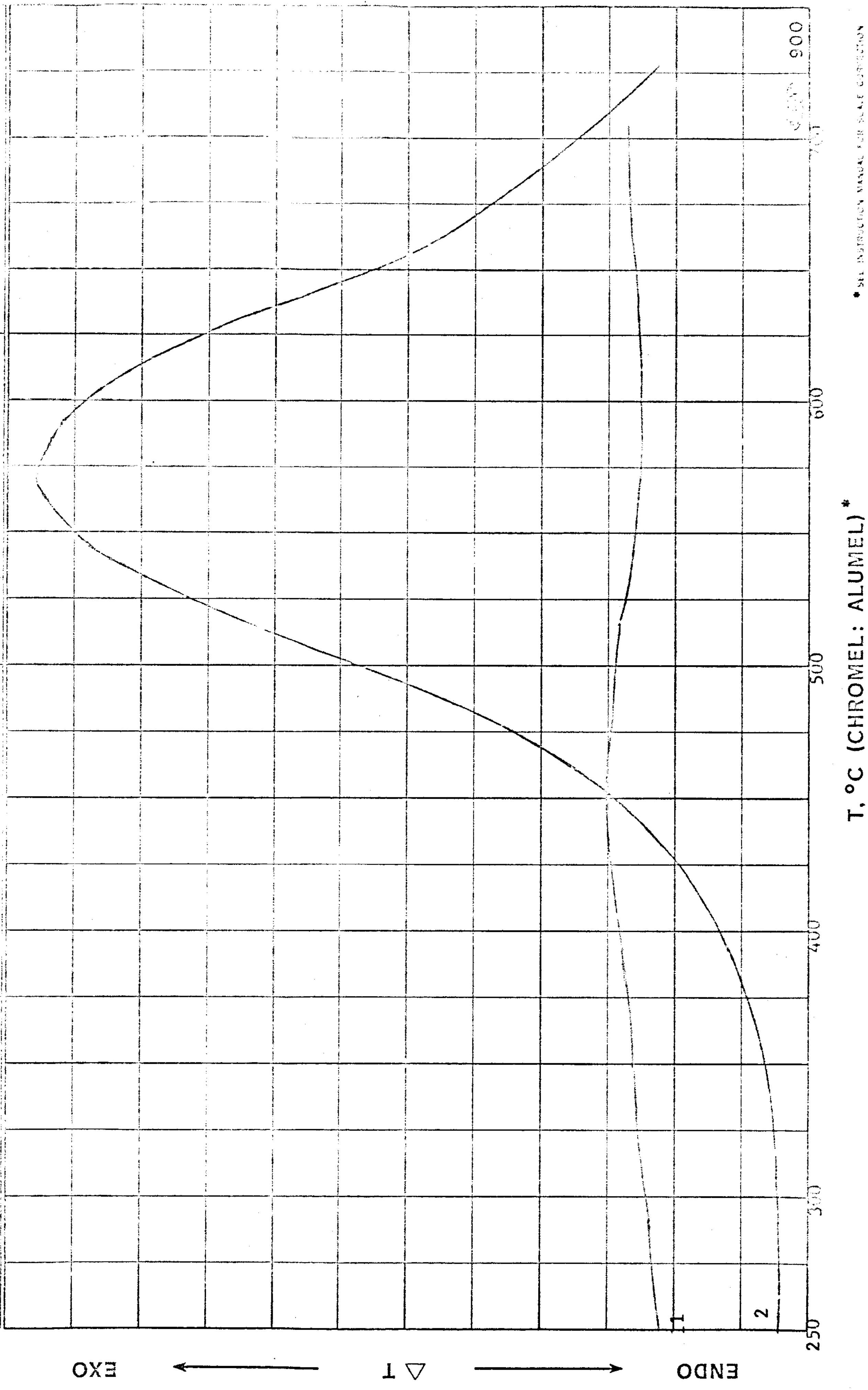
SHIFT IN. as req. IN.

RUN NO.

DATE 1-14-66

OPERATOR [illegible]

BASE LINE SLOPE 0



* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

DUPONT | INSTRUMENT PRODUCTS DIVISION

SAMPLE: [illegible]-62-13

$\{N-C_6H_4-$[illegible] $-C_6H_4-CH\}_n$

ORIGIN:

SIZE 3.2 m.

REF.

PROG. MODE heat

RATE 5 °C/MIN, START °C

ATM. air 1 Std 1/min. MM

	T	△ T
SCALE	50	1.0
SHIFT	0 IN.	as req. IN.

RUN NO.

DATE 1-14-66

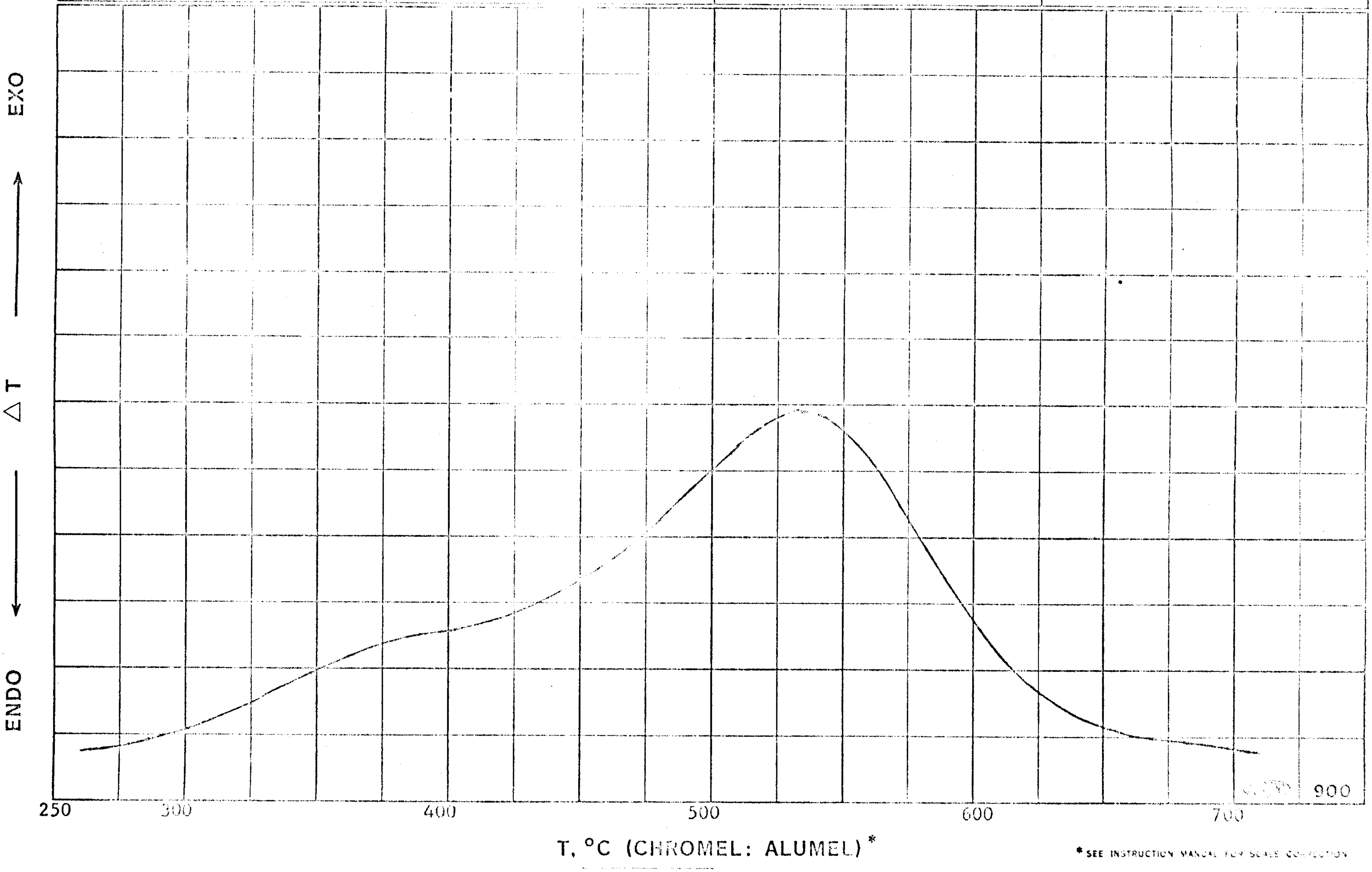
OPERATOR TD

BASE LINE SLOPE 0

SAMPLE:

RUN NO.:

Appendix No. 22



* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

INSTRUMENT PRODUCTS DIVISION

SAMPLE: RUN NO.: Appendix No. 23

SAMPLE: Pyrolitic Graphite

ORIGIN: NASA

SIZE 4.7 mg.

REF.

PROG. MODE heat

RATE 15 °C/MIN, START °C

ATM. 1) N_2 2) air , 1 Std 1/min MM

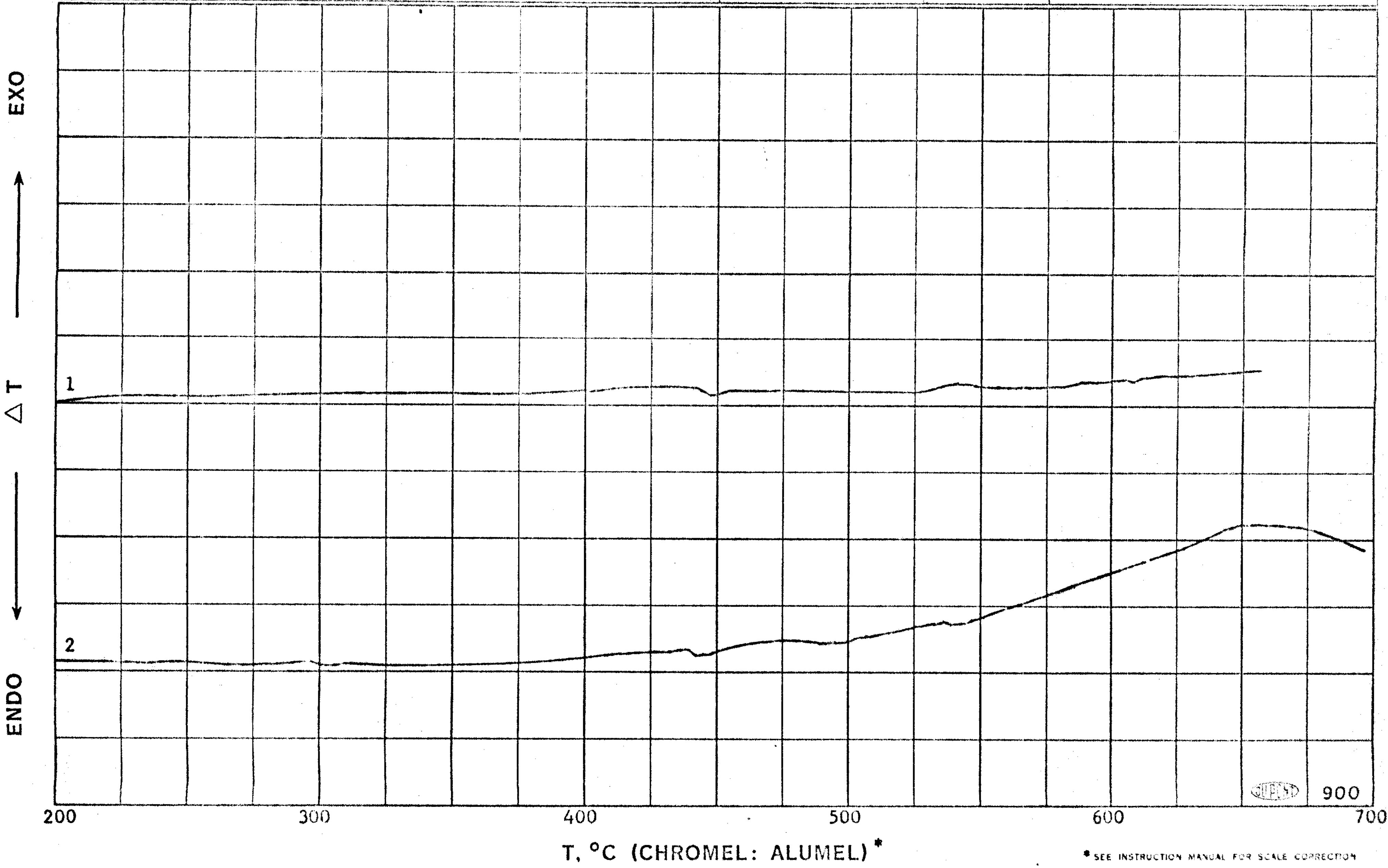
	T	△ T
SCALE	50 °C/IN.	1.0 °C/IN.
SHIFT	0 IN.	as req. IN.

RUN NO.

DATE 1-12-66

OPERATOR TD

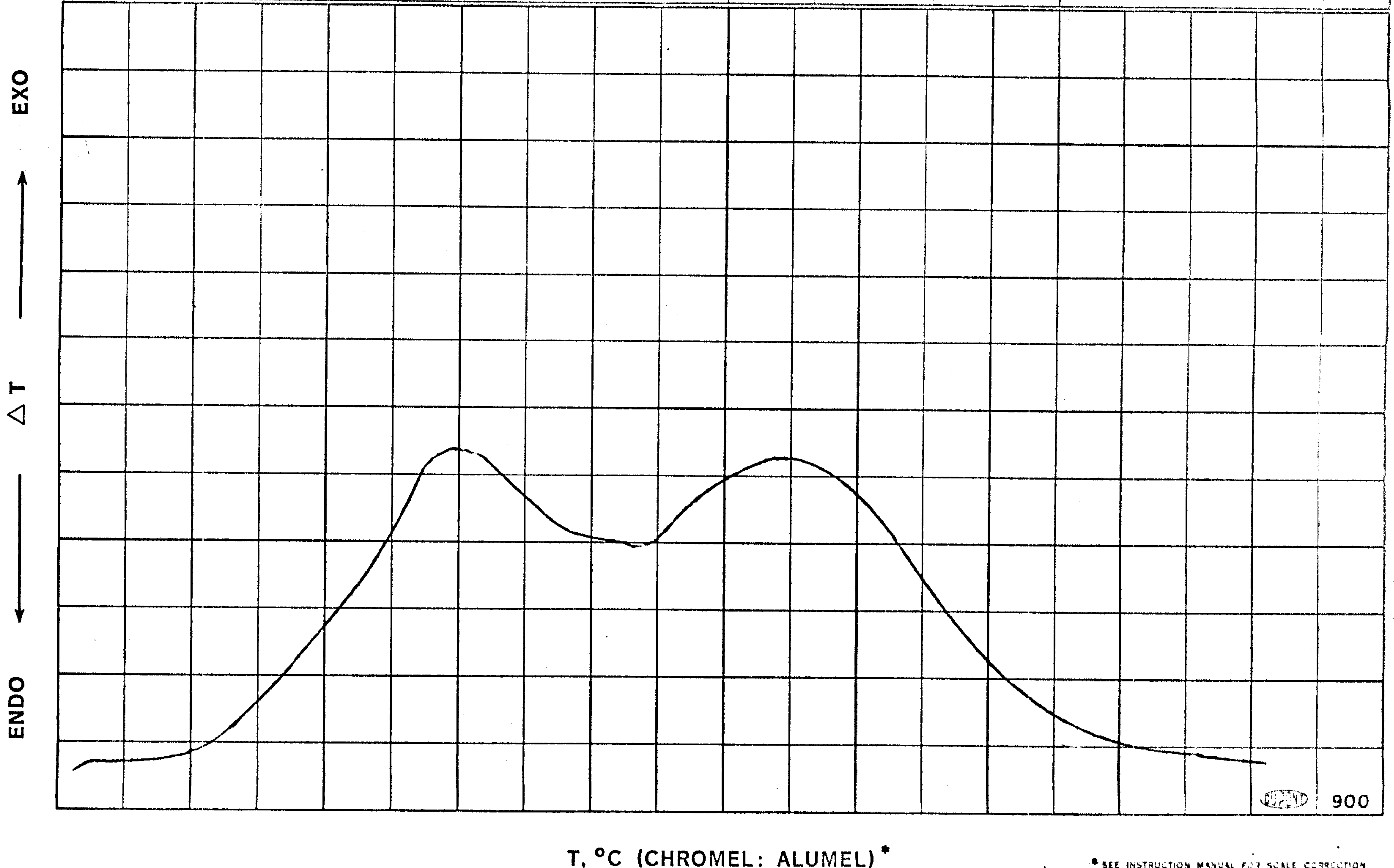
BASE LINE SLOPE 0



*SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

INSTRUMENT PRODUCTS DIVISION

SAMPLE: DA-42-94	SIZE 2.7 mg.	ATM. air MM		RUN NO.
$\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$	REF.	T	△ T	DATE 1-12-66
yellow polymer	PROG. MODE heat	SCALE 50 °C/IN.	1.0 °C/IN.	OPERATOR TD
ORIGIN:	RATE 5 °C/MIN, START °C	SHIFT 0 IN.	as req. IN.	BASE LINE SLOPE 2



* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

SAMPLE:

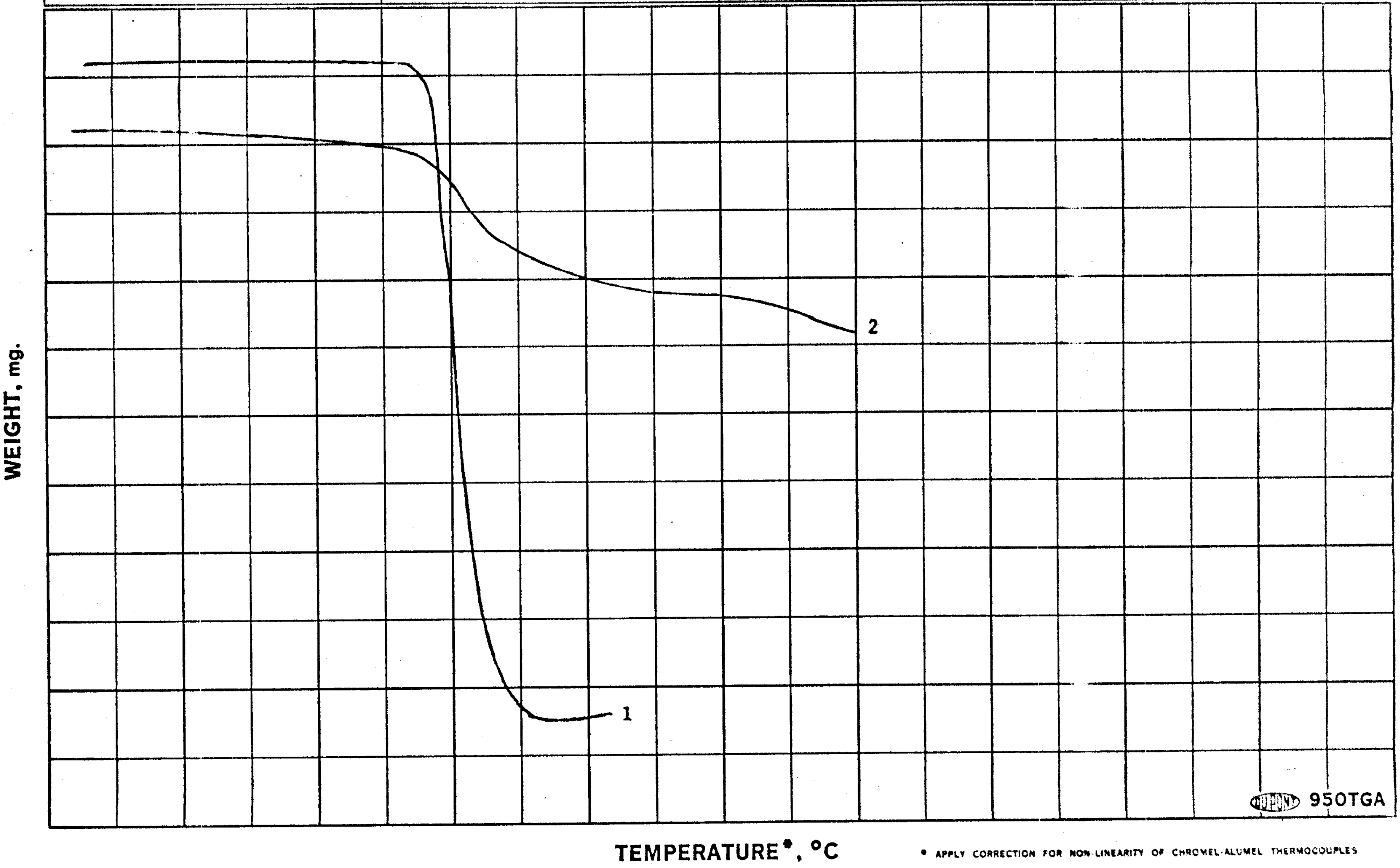
RUN NO.:

Appendix No. 24

Appendix No. 25

INSTRUMENT PRODUCTS DIVISION

SAMPLE: DA-42-13 $\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$ irradiated in vacuum 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 1-22-66. OPERATOR JVC HEATING RATE 15 °C/min. ATM. 1) air; 2) nitrogen TIME CONSTANT 2 sec.



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

DU PONT | INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-42-13-H600 $\{N-C_6H_4-N{=}HC-C_6H_4-CH\}_n$ irradiated in vacuum	**X-AXIS**	**Y-AXIS**	**RUN NO.** ____ **DATE** 1-22-66
	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) air; 2) nitrogen
SIZE 10 mg.	**TIME SCALE (ALT.)** 0	**SUPPRESSION** 0 mg.	**TIME CONSTANT** 2 sec.

Appendix No. 26

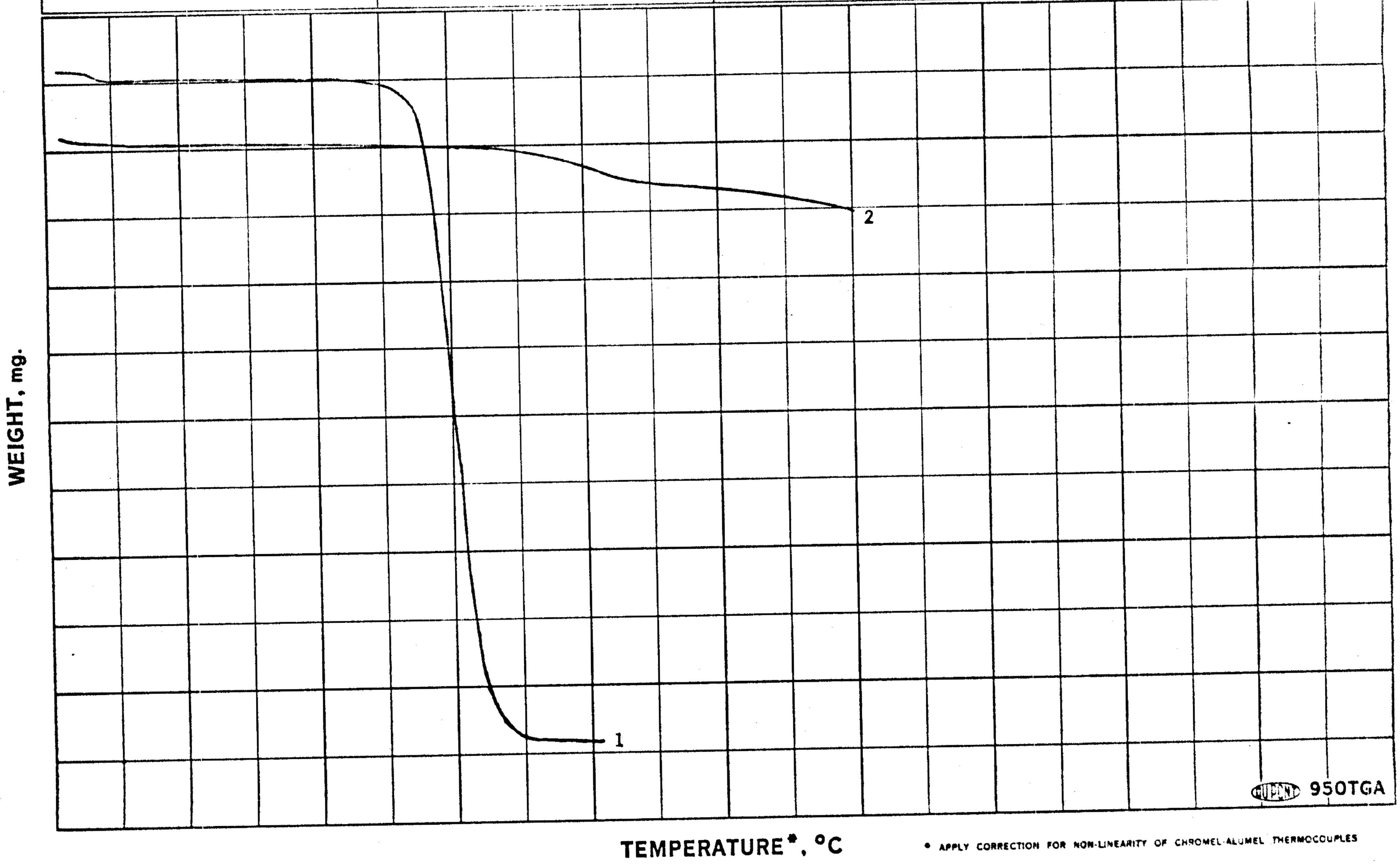
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-42-13	X-AXIS	Y-AXIS	RUN NO. ____ DATE 1-22-66
$\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR JVC
irradiated - sealed in air	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. 1) air; 2) nitrogen
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-42-13-H600 $\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$ irradiated - sealed in air 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 1-22-66 OPERATOR JVC HEATING RATE 15 °C/min. ATM. 1) air; 2) nitrogen TIME CONSTANT 2 sec.



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

Appendix No. 28

Appendix No. 29

SAMPLE: DA-42-13
$\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$
irradiated - open to air

SIZE 10 mg.

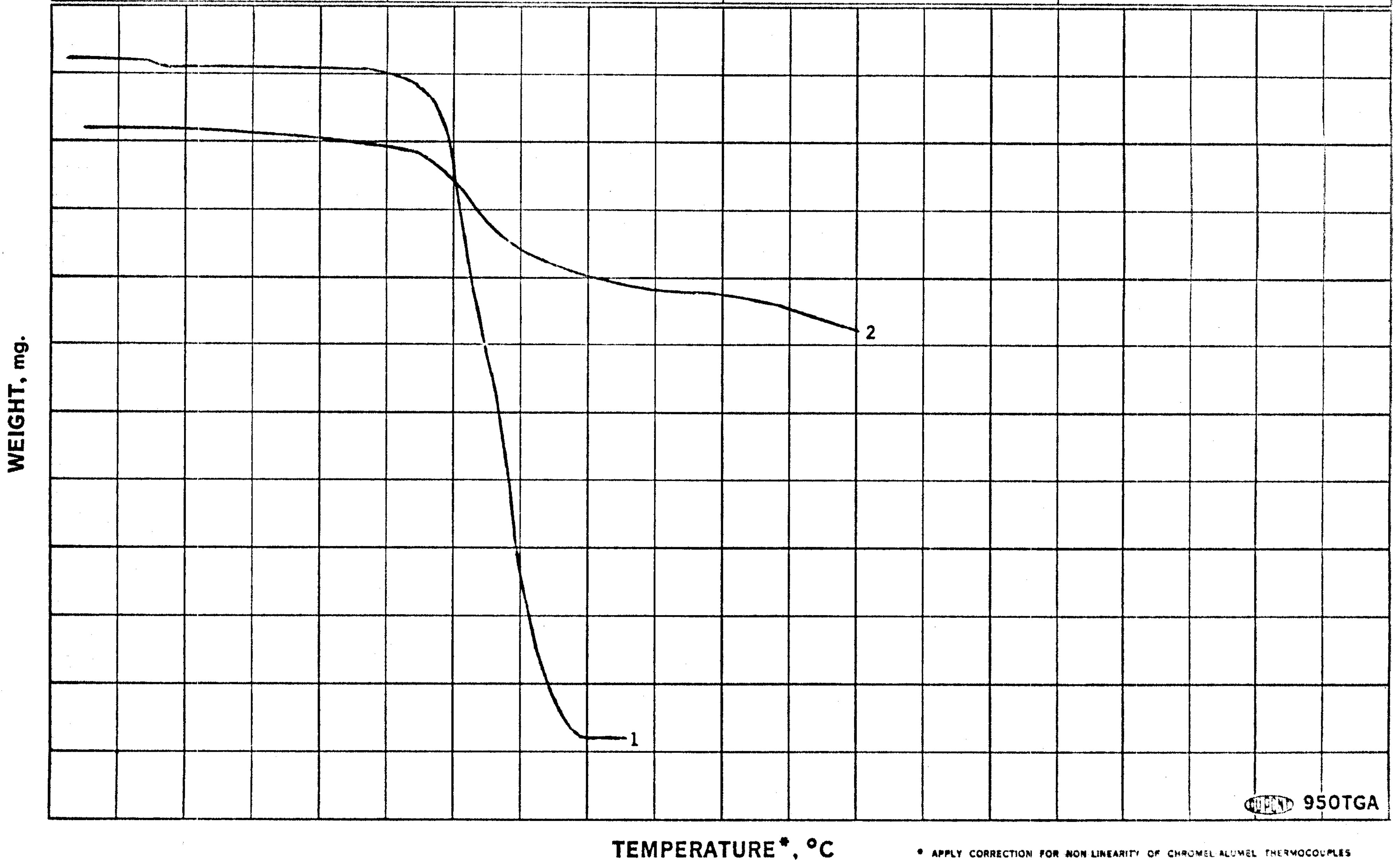
X-AXIS

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** 1-22-66
OPERATOR JVC
HEATING RATE 15 °C./min.
ATM. 1) air; 2) nitrogen
TIME CONSTANT 2 sec.

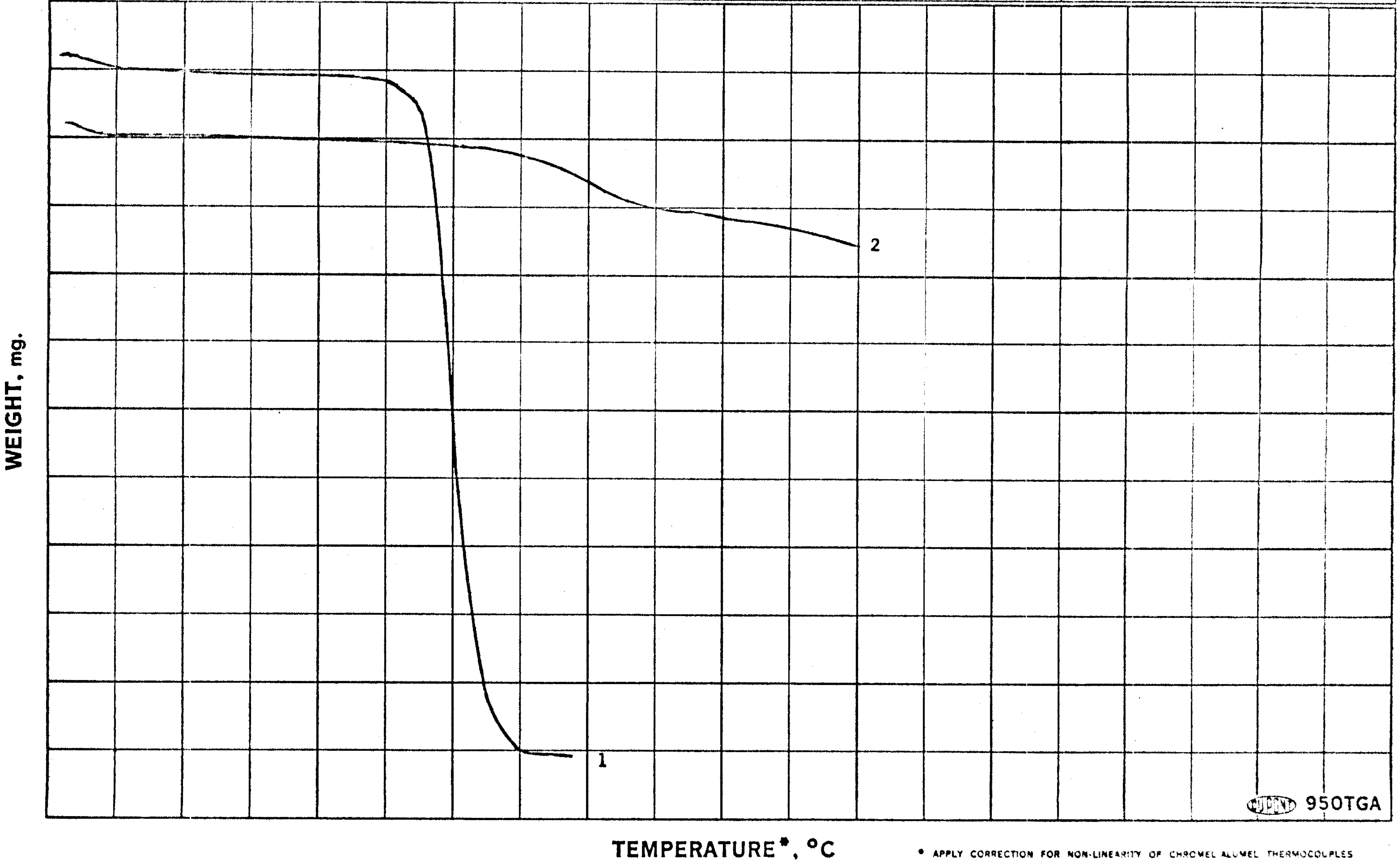


* APPLY CORRECTION FOR NON LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

DUPONT | INSTRUMENT PRODUCTS DIVISION

Appendix No. 30

SAMPLE: DA-42-13	X-AXIS	Y-AXIS	RUN NO. ____ DATE 1-22-66
$\{N-C_6H_4-N{=}HC-C_6H_4-CH\}_n$	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch	OPERATOR JVC
irradiated - open to air	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C./min.
			ATM. 1) air; 2) nitrogen
SIZE 10 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES