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ON THE

FUNDAMENTAL STUDIES ON THE SYNTHESIS OF HEAT-RESISTANT POLYMERS

THE SYNTHESES AND EVALUATION OF POLYMERIC AZINES

PERFORMED

UNDER

NASA GRANT NsG339

BY

G. F. D'ALELIO

PRINCIPAL INVESTIGATOR

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

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FOREWORD

This report is a summary report of the researches performed under NASA Grant NsG339 for the period 15 September 1965 to 31 January 1966 on the syntheses 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 and R. Schoenig.

Date: February 15, 1966

Signed: G. F. D'Alelio

G. F. D'Alelio
Principal Investigator

ABSTRACT

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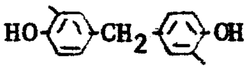
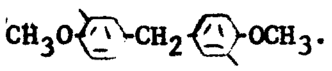
This report covers work performed on polyazine polymers of the general formula $\{HC\text{-}Ar\text{-}CH{=}N\text{-}N\}_n$ where Ar represents ,  and . These three azine polymers were prepared by the solution method, yielding infusible yellow brick-dust polymers, and by the melt method, yielding infusible, higher molecular weight black polymers. The azine polymers were shown to lose nitrogen upon heating and form a thermally stable polystilbene-type polymer. Therefore, thermoanalytical studies, employing thermal gravimetric analysis, differential thermal analyses and calorimetric analyses, were performed to monitor the parameters of the azine decomposition. Data on the weight-loss temperature ranges, the kinetics of decomposition and the extent of decomposition were obtained from the yellow polymers. Both the yellow solution and the black melt polymers were thermally evaluated by thermal gravimetric analyses to determine their relative stabilities in nitrogen and in air, both in relation to the method of synthesis and to the nature of the Ar moiety. The effect of particle size on thermal stability was simultaneously evaluated. Molecular weight determinations were performed on the yellow polymers by means of infrared studies, elemental analysis and viscometry; and an approximate $\overline{DP}$ for these yellow polymers obtained.

The polystilbenes derived from the polyazines possess high thermal stability in nitrogen and in air.

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I. Introduction.

In a previous report[1] there was summarized results of preliminary studies on the syntheses of polymeric azines, $\{\text{HC-Ar-CH=N-N}\}_n$ in which Ar represents a divalent aromatic moiety. Selected azine monomers were synthesized to serve as prototypes for the azine polymers; and the mechanism, kinetics, and decomposition temperatures of these monomers were investigated and reported.[1]

The conditions required for the synthesis of high molecular weight black azine polymers were established and used successfully to synthesize them by melt polymerization techniques.[1] It was also shown in the report[1] that these polymeric azines were in fact thermally unstable at temperatures in excess of 300°C and, by the very act of decomposition, produced successfully thermally stable stilbene polymers. These results indicated the need for more detailed investigations in several areas of this research.

The first area concerned a more detailed examination of the decomposition of the polymeric azines into polystilbenes, which was formulated[1] according to the reaction

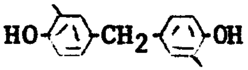
$$\{\text{HC-Ar-CH=N-N}\}_n \xrightarrow{\Delta} \{\text{HC-Ar-CH}\}_n + n\,H_2\uparrow \qquad \text{(eq. 1)}$$

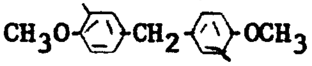
and on which the ablative properties of these polymers were predicted.[1] Thermoanalytical methods were used to study this decomposition; these methods included thermogravimetric analyses (TGA), differential thermal analyses (DTA), and calorimetric analyses (ΔH). These measurements were contemplated as yielding information on decomposition temperature ranges, phase changes, the kinetics of reactions and calorimetric values. To ascertain the influence of molecular weight on the thermal properties of the azine polymers, both low molecular weight yellow polymers and the higher molecular weight black polymers were scheduled for examination. Many of the thermal studies on the yellow polymers have been completed and are included in this report; corresponding studies on the black polymers have been initiated.

The second area concerned the effect on the thermal stabilities of the polymers with changes in the aromatic moiety, Ar, in the polymers of the structure $\{\text{HC-Ar-CH=N-N}\}_n$. The simplest polymer of this family is the one in which Ar is phenylene,  . It was believed that controlled changes in the polymer could be deliberately designed into the polymer by changing the nature of the Ar moiety. For example, if intramolecular bonding of one kind or another, could be introduced into the polymer chain, it might be possible to raise the decomposition temperature without destroying the ability of the polymer to eliminate nitrogen and still yield a polystilbene. Also, by modifying the structure by an appropriate solubilizing substituent, it might be possible to solubilize at least the yellow polymers, and thereby to utilize the solutions in measurements of such parameters as molecular weight.

In these studies, the phenylene group would serve as the reference aryl moiety.[1] The Ar moieties evaluated in this phase are the structures

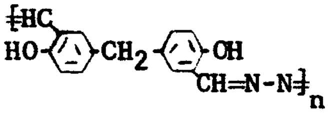
1. 

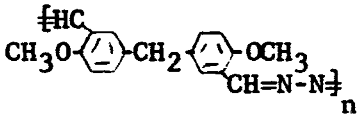
2. 

3. 

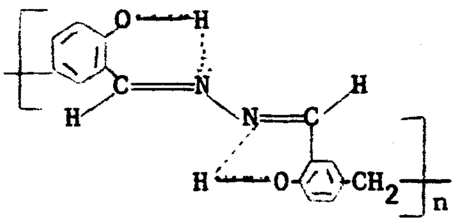
and their corresponding polymers are:

A. 

B. 

C. 

Polymer B was chosen to evaluate the effect of hydrogen bonding, -O---H---N-, a feature which becomes more apparent when that segment of the polymer is written as,



This type of hydrogen bonding should be destroyed readily by conversion of the hydroxyl function to another function. Accordingly, polymer C was chosen for this purpose as the comparison polymer. In this way, if any measurements indicated the presence of hydrogen bonding in No. 2, this value should be lowered in No. 3 and thereby offer convincing evidence of its existence.

The phenolic hydroxyl as a substituent,  , should also function to solubilize the polymer in aqueous solutions of alkali.

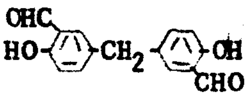
The presence of the -CH_2- linkage between the two benzene rings in both of these compounds should also give some indication of the effect on thermal stability of changes in the extent and character of conjugation. The presence of this -CH_2- linkage generates "pseudo conjugation" instead of interrupted conjugation.[2]

The preparation of polymers B and C necessitated the syntheses of their corresponding monomers and derivatives. Low molecular weight yellow polymers as well as high molecular weight polymers were synthesized and studied in this second area.

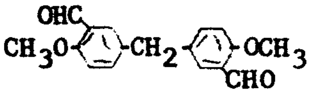
In the third area of study, efforts were made to determine the molecular weight of the azine polymers. Viscometry, elemental analyses, and infrared spectroscopy were the methods used.

II. <u>Syntheses of Monomers</u>.

The following monomeric dialdehydes were required for the polymerization with hydrazine:



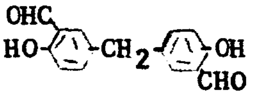
5,5'-methylene disalicylaldehyde (MDS)



5,5'-methylene dimethoxydisalicylaldehyde (MDMS).

They were prepared using the phenolformaldehyde-type condensation; then structures proven by NMR and by comparison with literature data.

A. Experimental.

1. (DA-39-71) Attempted Preparation of  (MDS).

Salicylaldehyde, 5.0 g. (0.04 M), was placed in a microflask chilled in ice. The flask was equipped with a magnetic stirrer and an inlet for nitrogen to provide an inert atmosphere. To the flask was added a mixture of 37% aqueous formaldehyde, 1.66 g. (0.02 M), and concentrated sulfuric acid, 0.15 g. The ice melted as the reaction proceeded; the mixture was allowed to stand overnight. No solid product was isolated from this mixture.

2. (DA-39-72) Attempted Preparation of MDS.

The procedure was the same as that used in DA-39-71, except that, when the ice had melted, the temperature was raised to 87°C. A black and infusible solid was recovered having the characteristics of a Bakelite resin.

3. (DA-39-74) Attempted Preparation of MDS.

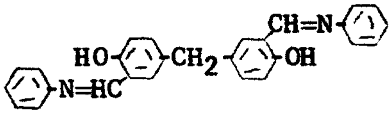
The procedure was the same as that used in DA-39-71, except that the acid concentration was increased to 7.9 g. Only a black tarry solid was recovered from this reaction.

4. (DA-39-82) Preparation of MDS.

Salicylaldehyde, 1.25 g. (0.010 M), acetic acid, 2.5 ml. as solvent, ans 37% aqueous formaldehyde, 0.42 g. (0.014 M), were mixed together in a

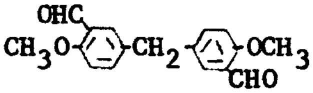
100-ml. round-bottom flask and placed in an ice bath. To this was added dropwise 5 ml. of concentrated sulfuric acid. The solution was a clear yellow after the sulfuric acid addition. As the ice melted and the solution warmed to room temperature, the mixture became cherry red and a solid formed. The solid was separated by suction filtration, 0.85 g. (47% of theoretical). The solid was recrystallized from xylene to give a cream-colored crystalline solid, m.p. 141-142°C, lit.[3] 140°C. NMR, Appendix No. 1, and IR, Appendix No. 2, were recorded.

5. (DA-39-83) Preparation of MDS-dianilide (MDSDA).



MDS, 20.00 g. (0.078 M) and aniline, 14.51 g. (0.156 M) were added to 200 ml. of benzene in a Dean-Stark apparatus. The benzene solution was refluxed until the theoretical amount of water was collected. The reaction was then cooled and the benzene removed by flash evaporation; an orange-yellow solid was recovered in quantitative yield. It was recrystallized from 95% ethanol to give an orange solid, m.p. 144-146°C. NMR, Appendix No. 3, and IR, Appendix No. 4 were recorded.

6. (DA-39-84) Attempted Preparation of (MDMS).



MDS, 1 g. (0.004 M), was added to a solution of sodium hydroxide, 0.48 g. (0.012 M) in 10 ml. of water. To the resulting yellow slurry dimethylsulfate, 2.5 g. (0.02 M), was added. The reaction was stirred at room temperature for two hours and then acidified with 1:1 concentrated hydrochloric acid: water, extracted with ether, the ether separated and dried. On evaporation of the ether only the starting product, MDS, was recovered.

7. (DA-39-85-b) Attempted Preparation of MDMS).

In a flask equipped with a magnetic stirrer and nitrogen inlet was added

MDS, 1 g. (0.004 M), to a solution of sodium hydroxide, 0.48 g. (0.012 M) in 10 ml. of water. To the resulting clear yellow solution methyliodide, 2.84 g. (0.02 M), was added. After two hours at room temperature, the solution became dark maroon in color. The solution was then extracted with ether, the ether evaporated and the desired product was not obtained.

8. <u>(DA-39-89) Preparation of MDMS.</u>

The following procedure was adopted from an allied preparation in Organic Synthesis.[4] MDS, 2.00 g. (0.0078 M) was added to 10 ml. of boiling water. A solution of sodium hydroxide, 2.76 g. in 11.04 ml. of water, was prepared. Of this alkaline solution 5.17 ml. was then added to the MDS-boiling water solution. A clear orange-red solution was obtained upon the sodium hydroxide addition. Dimethylsulfate (3.74 g.) was then added rather slowly; after ten minutes another addition (0.71 g.) of dimethylsulfate was made. After this last addition the yellow solution became acidic to litmus indicator. This was then followed by addition of 0.88 ml. of sodium hydroxide solution (solution again turned yellow). This stepwise addition is repeated twice more. After a final addition of 0.71 g. of dimethylsulfate, the solution was made alkaline by addition of 2.2 ml. of the sodium hydroxide solution. Total dimethylsulfate used: 6.31 g. (0.00246 M). The solution contained a yellowish precipitate. This precipitate was removed by filtration, washed with water several times and recrystallized from 95% ethanol. After drying, the solid was colorless, m.p. 130-131°C, and the yield was essentially quantitative. Its NMR, Appendix No. 5, and its IR, Appendix No. 6 were recorded.

B. Discussion.

Salicylaldehyde, being a phenol, has several positions on its aromatic nucleus which are activated toward electrophilic attack such as in the phenol-formaldehyde type condensation. Hence the possibility of condensation of one salicylaldehyde molecule with another through the formaldehyde methylene is high; and consequently Bakelite-type resins are obtained, especially at high temperatures. This reaction, therefore, complicates the synthesis of the bis compound in reaction of salicylaldehyde with formaldehyde. Dilution with acetic acid and low temperatures were found preferentially to aid the condensation of formaldehyde with salicylaldehyde to form the desired bis compound. The mechanistic part played by the acetic acid has not at the present been determined. No attempts were made to increase the reported yields, though all evidence indicates that they can be increased.

III. Syntheses of Polymers.[1]

Polymeric azines were prepared from the previously synthesized monomers. Both the yellow low molecular weight polymers and the higher molecular weight polymers were synthesized.

A. Experimental.

1. Solution Polymerization.

a. (DA-39-93) Polymerization of MDS and Hydrazine.

Under a nitrogen atmosphere, MDS, 10.00 g. (0.039 M), was dissolved in 100 ml. of refluxing benzene in a Dean-Stark apparatus. To this was added anhydrous hydrazine, 1.30 g. (0.039 M). Upon addition of the hydrazine the solution immediately became yellow and a yellow solid precipitated out. The reaction was stopped when no more water was collected in the trap. The reaction, after filtration, produced a yellow brick-dust polymer which was infusible. Yield was 88% of theoretical.

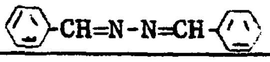
b. (DA-39-95) Polymerization of MDMS and Hydrazine.

In a nitrogen atmosphere, MDMS, 5.00 g. (0.018 M) was dissolved in 100 ml. of refluxing benzene in a Dean-Stark apparatus. To this solution was added anhydrous hydrazine, 0.565 g. (0.018 M). With the hydrazine addition the solution turned yellow and when no more water was collected the reaction was stopped and there was recovered after filtration a yellow brick-dust polymer which was infusible. Yield was 92% of the theoretical.

2. Melt Polymerizations.

a. (DA-39-97) Polymerization of MDSDA and $(H_5C_2)_2C{=}N{-}N{=}C(C_2H_5)_2$ (D-3-PA).

MDSDA, 1.0511 g. (0.0026 M), and D-3-PA, 0.4346 g. (0.0026 M), were placed in a microflask and the mixture heated in an inert nitrogen atmosphere. The temperature was raised slowly to 180°C and the solid mixture melted into a yellow-orange clear melt. It then progressed with time to dark-orange, red, reddish-brown, brown and dark-brown. Its viscosity increased until at the dark-brown stage it became extremely viscous. Then the pressure was reduced here to 20 mm. Hg and the by-products distilled over. After three hours at 180°C and 20 mm. Hg the reaction was stopped and 0.8327 g. of brown glossy polymer was retrieved (126% of theoretical). It was infusible and insoluble. Analysis for N_2 = 5.85%.[9]

b. (DA-39-99) Polymerization of MDMS and  (DBA).

MDMS, 1.0225 g. (0.0036 M), and DBA, 0.7489 g. (0.0036 M), were placed in a microflask and the mixture heated under an inert atmosphere in nitrogen. The temperature was raised slowly to 180°C; the solid mixture melted to an amber clear liquid then changed to dark orange, red, reddish-brown, brown, and dark-brown at which point the solution became viscous. The pressure was then reduced to 10 mm. Hg and the temperature maintained at about 175°C for ten hours. At this point the reaction was stopped and a dark-brown glossy polymer recovered (yield 115% of the theoretical). It was infusible and insoluble.

3. Discussion.

As had been observed before,[1] solution polymerization produced only the lower molecular weight yellow brick-dust polymers. The melt polymerizations yielded the high molecular weight darker colored polymers with yields exceeding 100% calculated on the basis of $n = \infty$ due probably to the retention of by-product Schiff base molecules and telomerization of the chains.[1,2]

IV. Thermal Analyses of Reactions of Polymeric Azines.

It has been known[5] for some time that monomeric azines of the general formula Ar-CH=N-N=CH-Ar' can be thermally decomposed into a number of products, the most plentiful of which is nitrogen. Both the kinetics[5] and the most probable mechanism[6] for this reaction have been reported. However, no similar study has been reported on the polymeric azines; and it was decided to examine this phenomenon in polymers. The techniques of thermal analyses used in this study included thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and calorimetric analysis (ΔH).

Thermogravimetric analysis can measure small weight losses in the polymer as a function of time and temperature; this information furnishes useful data such as temperature ranges of the weight-losses, the kinetics of the weight loss and the extent of the weight loss. In these studies, the du Pont 950 Thermogravimetric Analyzer was used to record the TGA thermograms. In these TGA's as well as in the subsequent measurements, the polymer was used in a powdered form. In those cases where solid glassy polymers were evaluated, they were reduced to powder by grinding in a stainless steel vibrator for sixty seconds.

In order to determine the weight-loss kinetics from the TGA thermograms, the method of Freeman and Carroll[7] was used to evaluate the rate parameters. Since this method of kinetic analysis involves the continual increase in sample temperature, the uncertainties due to the initial thermal lag associated with isothermal experiments are essentially eliminated. At the same time, the order of the reaction and the energy of activation may be obtained from one experimental curve. The method of Freeman and Carroll is based on the following derived expression applied by Anderson and Freeman.[8]

$$\log \quad (dw/dt) = x\triangle\log W_r - (\triangle E^{*}/2.3\ R)\triangle(1/T) \qquad \text{(eq. 1)}$$

where:

dw/dt = the rate of reaction

x = the order of reaction

$\triangle E*$ = the energy of activation

R = the gas constant

T = the absolute temperature

W_r = $\triangle W_c - \triangle W$ (proportional to the amount of reactant)

$\triangle W$ = the weight loss at the point where dw/dt is taken

$\triangle W_c$ = the total weight loss associated with a given reaction.

To evaluate the constants in equation 1, $\triangle$ log dw/dt is plotted against log W_r if $\triangle(1/T)$ is kept constant. The order of reaction, x, is determined from the slope and the energy of activation from the intercept at $\triangle \log W_r = 0$. A simple method of determining dw/dt and W_r at constant $\triangle(1/T)$ is to plot the first derivatives of the primary thermogravimetric curve and corresponding W_r as a function of reciprocal absolute temperatures.

Differential thermal analysis measures exotherms and endotherms as a function of temperature at a given heating rate. The DTA thermograms afford a more or less qualitative measure in the system of any physical or chemical changes large enough to register a heat gain or heat loss against a reference. In these studies, pyrolytic graphite obtained from NASA was used as the reference. In these studies the du Pont 900 Differential Thermal Analyzer was used to record the DTA thermograms.

Calorimetric analyses are closely allied to DTA except that they yield quantitative information. The calorimeter cell is essentially a bomb calorimeter which measures exotherms or endotherms of a known mass of sample and traces these changes in the form of a graph. The area under the curve of these traces is measured accurately with a polar planimeter and related to the ΔH of the reaction by the relationship of equation 2.

$$H = E \cdot \frac{A\Delta T_s \quad T_s}{M_a} \qquad \text{(eq. 2)}$$

where:

ΔH = m cal/mg. ± 5%

E = calibration coefficient, m cal/°C min.

A = peak area, sq. in.

ΔT_s = Y axis sensitivity setting, °C/in.

T_s = X axis sensitivity setting, °C/in.

M = sample mass, mg.

a = heating rate, °C/min.

The peak temperatures usually differ, to some extent, with those observed in the DTA and TGA thermograms. The values of ΔT_s, T_s, M, and a are those set by the experiment on the control panel of the du Pont 900 Thermal Analyzer. In these studies the du Pont Calorimetric Cell was used to record the ΔH thermograms. The calibration coefficient, E, of this cell is determined experimentally as a function of temperature by using metals of known heats of fusion and application of equation 2.

A. Thermal Analysis of Reactions of Yellow Polymers.

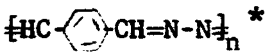
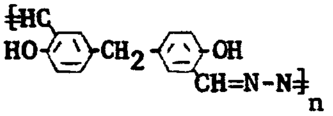
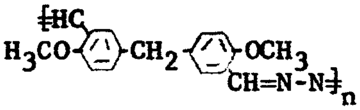
The high molecular weight black polyazines, because of possible monomer inclusion as well as loss of nitrogen due to conditions of synthesis, were not chosen, therefore, for primary study by these methods. The yellow polyazines prepared by the solution technique were studied first. This selection would allow, also, a better comparison of stabilities due to substitution in the polymers versus substitution in the monomers which have already been reported.[1]

1. TGA of Yellow Polyazines for Kinetic Studies.

The polymers selected for study are shown in Table 1, with the appendix number of their thermograms. The heating rate was 5°C/min. and pure nitrogen was used as the inert gas at a flow rate of one standard liter per minute.

Table 1

Polymers Used in TGA Studies

Polymer Designation	Polymer	Thermogram Appendix No.
DA-39-34		7
DA-39-93		8
DA-39-95		9

* Synthesis given in reference 1; analysis for nitrogen[9] 17.15% before heating to 1176°C and 0.73% after heating.

a. Kinetic Data from Thermograms.

The method of Anderson and Freeman[8] was used to calculate dw/dt and W_r as shown in Appendix No. 10 for the polymer DA-39-34 from the data of the thermogram of Appendix No. 7. The values of dw/dt and W_r were then taken at equal intervals of 1/T of 1.0×10^{-5} $°K^{-1}$. The kinetic plot for this process is shown in graph form as Appendix No. 11.

The initial points of the reaction up to 280°C are those of zero order kinetics. The temperature dependency plot of this stage of the reaction is shown in graph form as Appendix No. 12. The energy of activation was calculated from the slope of this plot:

$$\overset{o}{\cancel{x}} \triangle \log W_r - \triangle(1/T) \quad \frac{\triangle E^*}{(2.3)(R)} = \overbrace{\triangle \log (dw/dt)}^{\text{slope}} \qquad \text{(eq. 3)}$$

by substitution,

$$\frac{-1 \times 10^{-5}}{°K} \cdot \frac{\triangle E^*}{(2.3)(1.98)} = 1.64 \times 10^{-3} \qquad \text{(eq. 4)}$$

then,

$$\triangle E^* = 11.5 \text{ kcal/mole} \qquad \text{(eq. 5)}$$

In the temperature range of 280°C to 370°C, there appears to be a transition from zero order to first order; however, the reaction is definitely first order in the range of 370-405°C as seen on Appendix No. 11. The energy of activation for this first order stage of the reaction is calculated from the extrapolated intercept at $\triangle \log W_t \times 10^2 = 0$; then, by substitution in equation 3,

$$-\frac{1 \times 10^{-5}}{°K} \cdot \frac{\triangle E^*}{(2.3)(1.98)} = -5.4 \times 10^{-2} \qquad \text{(eq. 6)}$$

then,

$$\triangle E^* = 24.7 \text{ kcal/mole} \qquad \text{(eq. 7)}$$

The reaction course at temperatures above 410°C seems to be a returning to zero order kinetics, indicating that the reaction responsible for the first order kinetics is substantially completed.

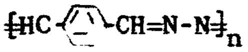
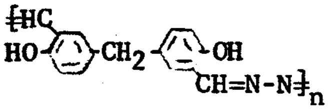
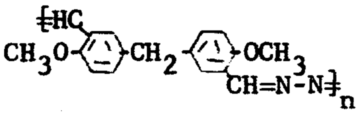
The thermal data on the two other yellow polymers, DA-39-93 and DA-39-95, have been obtained and their kinetic interpretation is presently underway.

2. <u>DTA of Yellow Polymers</u>.

The polymers selected for study are shown in Table 2 which also gives the appendix number of the thermograms. A heating rate of 15°C/min. and nitrogen gas flow rate of 2 standard cubic feet per hour were used as the best conditions.

Table 2

DTA of Yellow Polyazines

Polymer Number	Polymer	Thermogram Appendix No.
DA-39-34*		13
DA-39-93		14
DA-39-95		15

* Synthesis given in reference 1.

Each thermogram contains four distinct traces representing four different conditions of evaluation, namely:

Curve A = Original sample in nitrogen to 1176°C

Curve B = Recycle of sample A in nitrogen to 1176°C

Curve C = Recycle of sample A in air

Curve D = Original sample in air.

These DTA thermograms show, in Curve A, that a phase change does occur when the original sample is heated to 1176°C in nitrogen but that once having been heated thusly no further salient changes appear in the polymer when recycled in nitrogen to 1176°C again. That is, the polystilbene resulting from thermal decomposition is indeed different from the azine polymer in that the derived polymer is stable in nitrogen up to at least 1176°C. Also this polystilbene type polymer is more thermally stable in air than the polyazine as seen by comparing Curves C and D. It is interesting to note the broad but perceptible exotherms of Curves A which follow the main decomposition exotherms at about 350°C. They appear to have their maxima at about 880°C. This fact, coupled with the increased thermal stability after cycling in nitrogen, as well as the fact that the originally yellow polymers became brown upon heating, suggests that further chain lengthening has also occurred. Further, this chain lengthening should increase the thermal stability; it also should show a broad exotherm since end chain condensations take place slowly over a wide elevated temperature range. The resulting increase in conjugation causes the change in color of the polymer from yellow to brown or darker color. Furthermore, the TGA's also indicate a broad gradual weight loss out to 1176°C which could be attributed to further condensation and elimination of small by-product molecules.

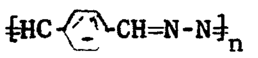
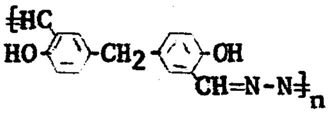
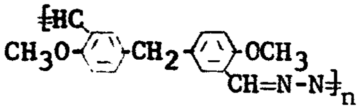
3. △H Determination.

a. Original Polymers in Nitrogen.

The polymers selected for study are shown in Table 3 which also gives the appendix numbers of the thermograms. A heating rate of 10°C/min. and a nitrogen gas flow rate of (1) one standard liter per minute were used as the best conditions.

Table 3

Polymers Used in △H Studies

Polymer Number	Polymer	Thermogram Appendix No.
DA-39-34		16
DA-39-93		17
DA-39-95		18

The exotherm peaks in the △H thermograms are in good agreement with those found in the DTA thermograms and in fair agreement with those in the TGA thermograms. Exothermic decomposition peaks are clearly evident in thermograms numbered 16, 17 and 18. The data of these thermograms were used to calculate the ΔH values and they are summarized in Table 4.

Table 4

ΔH for Yellow Polymers

Polymer	Nature of Peaks	Max. Temp. °C of Peak	ΔH in cal/mg
DA-39-34 Appendix No. 16	1. sharp 2. sharp	336 373	100 148
DA-39-93 Appendix No. 17	1. very broad 2. sharp	295 393	65 50
DA-39-95 Appendix No. 18	1. sharp 2. broad	328 425	145 40

The correlation of the calorimetric data with TGA data is awaiting the completion of the kinetic analyses of Polymers DA-39-93 and DA-39-95.

b. Derived Polystilbene in Air.

Since the polyazines yield polystilbenes on decomposition, it would be expected that with this transformation changes would occur in ΔH. Further, treatment of the polyazine and the polystilbene in nitrogen to 1176°C could infer that either the polyazine or polystilbene had graphitized. In such a case, ΔH and the peak temperatures of the polymers and of pyrolytic graphite should be comparable. Accordingly samples of the same three yellow polymers which were used to determine ΔH values in nitrogen were heated in nitrogen at a rate of 15°C/min. to 1176°C in the thermogravimetric apparatus to cause nitrogen elimination. These post-heated treated polymers are designated as such by the appendix number 1176; thus DA-39-34-1176 is polymer DA-39-34 which has been heated in nitrogen to 1176°C. As a reference pyrolytic graphite was evaluated in a similar way.

Table 5 lists the polymers evaluated with the appendix number of their thermograms and the calculated ΔH values.

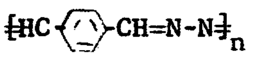
Table 5

△H in Air for Derived Polystilbenes

Polymer	Nature of Peak	Maximum Temp. of Peak, °C	△H kcal/g
DA-39-34-1176 Appendix No. 19	sharp	477	1.19
DA-39-93-1176 Appendix No. 20	sharp	509	1.35
DA-39-95-1176 Appendix No. 21	sharp	490	2.38
Graphite - 1176 Appendix No. 22	sharp	670	0.85

To some measure, the curves in thermograms of Appendix Nos. 19, 20 and 21 resemble the thermogram of graphite, Appendix No. 22, except that the peak temperatures are somewhat lower. It is expected that when the higher molecular weight black polymers are evaluated in a similar way, that the peak temperatures will shift to higher temperatures. In fact, the temperatures recorded for the yellow polymers are remarkably high.

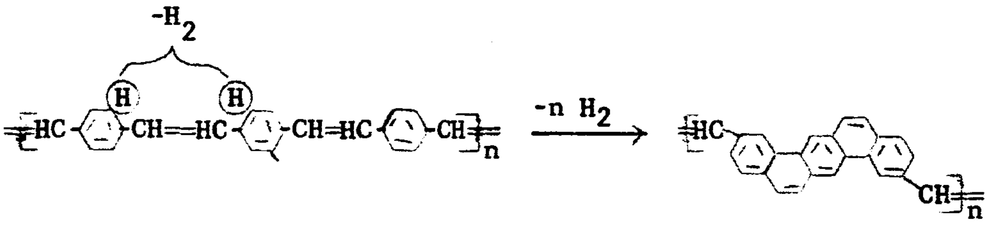
4. Discussion.

The TGA,DTA, and △H data for the yellow parent polymer, DA-39-34,  lead to the following description of its thermal reaction in a nitrogen atmosphere. This polymer begins to lose weight gradually starting at about 175°C and continuing to 285°C. In this temperature interval there is no evidence of either an exotherm or endotherm and the kinetics appear to be essentially zero order with a relatively low E_a of 11.5 kcal/m. This could be attributed to the loss of low molecular weight species from the polymer as the result of a process which involves a diffusion-controlled reaction through the solid polymer.

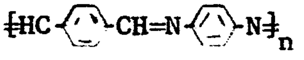
In the temperature range of 285-369°C a transition from zero order to first order is evident. In this region both the DTA and the calorimetric data show the onset of exotherms, that is, decomposition to nitrogen has started. This and residual zero order vaporization of low molecular weight species mentioned before lead to a mixed reaction order. The TGA shows also a definite multiple change in slope in this temperature region.

In the range of 369°C to 405°C, the decomposition reaction predominates and is first order with E_a equal to 24.7 kcal/mole. The DTA and $\triangle H$ thermograms show two closely spaced exotherms; the TGA indicates a sharp change in slope with a 16.4% weight loss. This weight is in agreement with the value of 17.15% nitrogen found in the polymer before thermal decomposition and a value of 0.75% nitrogen found after such decomposition.[9]

Beginning at 425°C and continuing to 1176°C, there appears to be a gradual leveling out of the weight loss slope. The DTA indicates a very slight and very broad exotherm which may be due to chain lengthening by chain-end coupling as well as possibly to thermal rearrangements of the following type:



(eq. 8)

Similar thermal and photochemical rearrangements of stilbene[10] and its nitrogen analogue benzalaniline[11,12] have been reported. It has been reported[13] also that when the poly Schiff base, , was heated to 800°C, hydrogen was detected by mass spectrum in the gaseous by-products. That this reaction should occur primarily at elevated temperatures is not difficult to rationalize, because the double bond in the polystilbene would have to rearrange thermally from the more stable trans configuration to the less favorable cis configuration before ring closure could occur. This process would require a high activation energy such as readily supplied only by high temperatures.

The foregoing results, combined with studies on the nature of the decomposition products should lead to the proposal of a suitable mechanism for the reaction processes involved.

V. Evaluation of Thermal Stabilities by TGA.

It is one of the purposes of this project to synthesize polyazines, which at some stage of synthesis are tractable and fusible. The melt polymerization technique has been shown[1] to yield intermediate black fusible polymers in contrast to the solution method which affords infusible, intractable brick-dust yellow polymers.[1] It is important to ascertain that, in the infusible state, the black polymers have thermal stabilities comparable to those of the yellow polymers. Accordingly TGA thermograms were obtained for both yellow and black polyazines.

A heating rate of 15°C/min. and a flow rate of one (1) standard liter per minute of nitrogen or of air were used in these measurements.

A. TGA of a Yellow Polymers.

The yellow polymers, previously prepared by the solution method were used for TGA measurements and are shown in Table 6, together with the appendix number of the thermograms. Three curves are shown on each thermogram. Curve 1 shows the weight losses as a function of temperature for the original yellow polymer when heated in nitrogen. Curve 2 shows the weight loss against temperature for the polymer of Curve 1 after the polymer has been heated to 1176°C, in nitrogen, allowed to cool in nitrogen and heated again in nitrogen on a recycle to 1176°C. Curve 3 is the thermogram for the polymer of Curve 2 which had been allowed to cool in nitrogen and reheated in air.

Table 7 gives the percentage weight loss of the yellow polymers of Table 6 on being heated in nitrogen.

Table 6

Yellow Polymers Used in TGA Measurements and Their Thermograms

Polymer Number	Appendix No. -- Curve Number		
	Heated in Nitrogen	Recycle in Nitrogen	Heated in Air After Recycle in Nitrogen
DA-39-34	23 - 1	23 - 2	23 - 3
DA-39-93	24 - 1	24 - 2	24 - 3
DA-39-95	25 - 1	25 - 2	25 - 3
DA-39-34*	26 - 1	26 - 2	26 - 3

* Heating rate in this case was 5°C/min.

Table 7

Percentage Weight Loss of Yellow Polymers at Various Temperatures While Being Heated in Nitrogen at 15°C/min.

Polymer Appendix No. : Curve	Per Cent Weight Loss at °C										
	200	300	400	500	600	700	800	900	1000	1100	1176
DA-39-34 Appendix No. 23-1	0.8	2.4	19.3	36.9	47.3	55.0	58.5	59.0	60.0	61.0	62.0
DA-39-93 Appendix No. 24-1	0.0	0.1	1.5	14.4	24.1	35.9	44.0	45.0	47.0	49.0	50.7
DA-39-95 Appendix No. 25-1	0.5	1.5	4.0	16.0	44.0	56.0	60.0	62.0	63.0	64.0	64.5
DA-39-34* Appendix No. 26-1	0.0	3.4	12.8	40.2	52.0	60.0	63.0	64.0	65.5	----	----

* heating rate in this case 5°C/min.

A comparison in the weight losses of these first three polymers of Table 7 is given in the thermogram, Appendix No. 27.

Table 8 gives the percentage weight-loss of the yellow polymers while the polymers of Table 7 are recycled in nitrogen.

Table 9 gives the percentage weight losses of the yellow polymers when the polymers of Table 8 heated twice in nitrogen were heated in air.

A comparison of the weight losses of the polymers of Table 9 is given in the thermogram Appendix No. 28.

Table 8

Percentage Weight Loss of Yellow Polymers on Recycling in Nitrogen

Polymer Appendix No. : Curve	Per Cent Weight Loss at °C										
	200	300	400	500	600	700	800	900	1000	1100	1176
DA-39-34 Appendix No. 23-2	0	0	0	0	2.5	2.5	2.5	2.5	2.5	5.0	5.0
DA-39-93 Appendix No. 24-2	0	0	0	0	0	0	0	0	0	0	1.0
DA-39-95 Appendix No. 25-2	0	0	0	0	0	0	0	0	0	0	1.0

Table 9

Percentage Weight Losses in Air of Yellow Polymers Which Had Been Recycled in Nitrogen

Polymer Appendix No. : Curve	Per Cent Weight Loss at °C						
	200	300	400	500	600	700	800
DA-39-34 Appendix No. 23-3	0	0	0	5.5	16.8	94.5	100.0
DA-39-93 Appendix No. 24-3	0	0	0	1.0	20.2	100.0	-----
DA-39-95 Appendix No. 25-3	2.2	2.6	3.8	5.0	9.5	95.0	100.0

Thermograms of the three yellow polymers were also obtained in air using the polymers directly prepared without previous heating or recycling in nitrogen. Table 10 gives the percentage weight loss of the "as is" yellow polymers when heated at 15°C/min. in air at a flow rate of one (1) standard liter per minute.

A comparison of the weight loss of the polymers of Table 10 is given in Thermogram Appendix No. 32.

Table 10

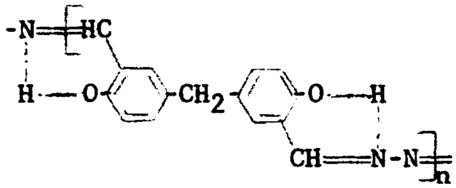
Percentage Weight Losses of Yellow Polymers
When Heated, as Prepared, in Air

Polymer	Per Cent Weight Loss at °C					
Appendix No.	200	300	400	500	600	700
DA-39-34 Appendix No. 29	0	2.5	12.0	55.0	90.0	100.0
DA-39-93 Appendix No. 30	0	2.0	3.0	28.0	94.0	100.0
DA-39-95 Appendix No. 31	0	2.0	12.0	26.0	85.0	100.0

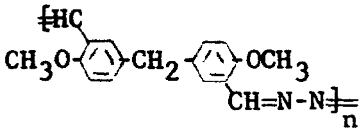
1. Discussion.

a. Thermal Stability of Yellow Polymers in Nitrogen.

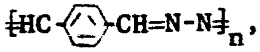
It is evident from thermograms, Appendix Nos. 23-1, 24-1, 25-1 and 25-2 and Table 7 that polymeric DA-39-93 is the most stable of the three polymers with respect to the temperature at which major nitrogen elimination occurs. Undoubtedly this is due to the increased stability of this azine polymer as the result of hydrogen bonding of phenolic (OH) with the azine nitrogen, thus:



The next most stable with regard to nitrogen elimination is DA-39-95, the methoxy derivative of the phenolic polymer,



The lower elimination temperature indicates that the hydrogen bonding present in the phenolic polymer has been reduced. However, since the methoxy polymer has a higher elimination temperature than the unsubstituted parent polymer

DA-39-34, , it may imply that some measure of hydrogen bonding still occurs between the hydrogens of the methoxy group and the azine nitrogen. This data is in good agreement with the results obtained on the nitrogen elimination of azine monomers.[1] It is very interesting to note that the weight-loss temperature curve was not altered appreciably when the heating rate was decreased from 15°C/min. (Appendix No. 23-1) to 5°C/min. (Appendix No. 26-1).

b. Thermal Stability of Polymers Recycled in Nitrogen.

Thermograms, Appendix Nos. 23-2, 24-2, and 25-2 and the data of Table 8 show that once the nitrogen has been eliminated from these polymers, and chain end coupling and other reactions have been completed in nitrogen, the derived polystilbene-type polymers suffer little weight loss on reheating and they show stability in nitrogen to at least 1176°C.

c. Thermal Stability in Air of Polymers Recycled in Nitrogen.

Thermograms Appendix Nos. 23-3, 24-3, 25-3 and 28, and Table 9 show that the three polystilbene-type polymers derived from the yellow polyazines all decompose in air in the range 600-650°C. The decomposition curve is smooth and inflectionless and is due to the methodic combustion of the organic material of the polymers.

d. Thermal Stabilities in Air of Polymers as Synthesized and Without Preheating in Nitrogen.

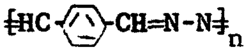
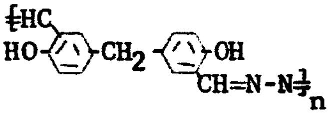
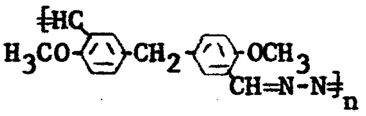
Thermograms Appendix Nos. 29, 30, 31, and 32 show that for this process the three polyazine polymers undergo a combination of decomposition and combustion and that there is no major difference among them since weight losses began to appear at about 350°C. The methoxy polymer and the unsubstituted polymer both exhibit comparable stabilities with the phenolic polymer somewhat less stable under these conditions. This data also indicated that the polymers produced after nitrogen elimination are much more stable in air than the polyazines from which they were derived.

B. TGA of Black Polymers.

The evaluation of the thermal stabilities of the black polyazines paralleled substantially the studies of the yellow polymers. The list of polymers studied and their corresponding thermograms are shown in Table 11. The synthesis of polymer DA-39-45 is given in a previous report.[1] Each thermogram shows three curves. Curve 1 shows the weight losses as a function of temperature for the original black polymers when heated in nitrogen. Curve 2 shows the weight-loss for the polymer of Curve 1 after the polymer had been heated in nitrogen to 1176°C, allowed to cool in nitrogen and heated again in nitrogen on a recycle to 1176°C. Curve 3 is the thermogram for the polymer of Curve 2 which was allowed to cool in nitrogen and reheated in air.

Table 11

Black Polymers Used in TGA Measurements and Their Thermograms

Polymer	Polymer Number	Appendix No. - Curve No.		
		Heated in Nitrogen	Recycled in Nitrogen	Heated in Air after Recycle in Nitrogen
	DA-39-45(a)-p	33-1	33-2	33-3
	DA-39-45(a)-m	34-1	34-2	34-3
	DA-39-97	35-1	35-2	35-3
	DA-39-99	36-1	36-2	36-3

The two polymers, DA-39-45(a)-p and DA-39-45(a)-m are the same polymer; the first with the appended designation -p means that the polymer was reduced to a powdered form whereas DA-39-45(a)-m, the polymer was in the form of a single mass or chunk. All other polymers except DA-39-45(a)-m were evaluated as powders. It has been estimated[2] that 10 mg. of solid polymer is reduced to about 500 particles by a grinding time of five seconds in a stainless steel capsule.

Table 12 gives the percentage weight losses of the yellow polymers of Table 11 on being heated in nitrogen.

Table 12

Percentage Weight Loss of Black Polymers at Various Temperatures While Being Heated in Nitrogen at 15°C/min.

Polymer Appendix No.	Per Cent Weight Loss at °C										
	200	300	400	500	600	700	800	900	1000	1100	1176
DA-39-45(a)-p Appendix No. 33-1	0.0	0.0	1.0	8.1	35.4	45.5	48.0	49.5	50.5	51.5	52.8
DA-39-45(a)-m Appendix No. 34-1	1.0	1.5	2.0	4.1	12.2	22.4	26.6	27.5	28.2	29.0	30.0
DA-39-97 Appendix No. 35-1	0.0	1.0	2.0	24.0	56.0	64.0	67.0	68.0	68.1	69.0	70.0
DA-39-99 Appendix No. 36-1	0.0	0.8	1.5	12.0	31.0	41.0	44.5	45.7	46.0	46.5	47.0

A comparison of the weight losses of the polymers of Table 12 is given in Thermogram Appendix No. 37.

Table 13 gives the percentage weight-loss of the black polymers of Table 12 recycled in nitrogen.

Table 13

Percentage Weight Loss of Black Polymers on Recycling in Nitrogen

Polymer Appendix No.	Per Cent Weight Loss at °C										
	200	300	400	500	600	700	800	900	1000	1100	1176
DA-39-45(a)-p Appendix No. 33-2	0	0	0	1.0	1.0	1.0	1.0	1.0	2.0	2.0	2.0
DA-39-45(a)-m Appendix No. 34-2	0	0	0	0	0	0	0	0	0	0	1.0
DA-39-97 Appendix No. 35-2	0	0	0	0	0	1.0	2.0	2.0	2.0	2.0	2.0
DA-39-99 Appendix No. 36-2	0	0	0	0	0	0	1.0	1.0	1.0	1.0	1.0

Table 14 gives the percentage weight losses of the black polymers of Table 13, which had been heated twice in nitrogen, heated in air.

Table 14

Percentage Weight Losses in Air of Nitrogen Recycled Black Polymers

Polymer Appendix No.	Per Cent Weight Loss at °C								
	200	300	400	500	600	700	800	900	1000
DA-39-45(a)-p Appendix No. 33-3	0.9	2.0	2.9	3.9	25.5	100.0	-----	----	-----
DA-39-45(a)-m Appendix No. 34-3	0	0	0	0	1.4	15.4	63.2	94.0	100.0
DA-39-97 Appendix No. 35-3	0	0	0	0	3.2	77.5	100.0	----	-----
DA-39-99 Appendix No. 36-3	0	0	0	1.8	13.0	100.0	-----	----	-----

A comparison of the weight-losses of the polymers of Table 14 is given in thermogram Appendix No. 38.

The thermograms of the three black polymers as they were prepared directly without previous heating or recycling in nitrogen were obtained in air. Table 15 gives the percentage weight-losses of the black polymers when heated at 15°C/min. in air at a flow rate of one (1) standard liter per minute.

Table 15

Percentage Weight Losses of Black Polymers
When Heated, as Prepared, in Air

Polymer Appendix No.	Per Cent Weight Loss at °C							
	200	300	400	500	600	700	800	900
DA-39-45(a)-p Appendix No. 39	0	0	1.5	16.3	94.0	100.0	----	-----
DA-39-45(a)-m Appendix No. 40	0	0	0	4.8	12.0	38.0	84.5	100.0
DA-39-97 Appendix No. 41	0	0	2.0	9.0	43.0	100.0	----	-----
DA-39-99 Appendix No. 42	0	0	8.7	35.0	98.0	100.0	----	-----

A comparison of the weight-losses of the polymers of Table 15 is given in Thermogram Appendix No. 43.

1. Discussion.

a. Thermal Stabilities of Black Polymers in Nitrogen.

The data of Table 12 and thermograms Appendix Nos. 33-1, 34-1, 35-1, 36-1 and 37 show that of these black polymers the regular azine, DA-39-45(a)-p and the methoxy polymer, DA-39-99, are very similar. The hydroxy polymer, DA-39-97, is somewhat less stable losing about 70% of its weight at 1176°C. It should be pointed out, however, that the yields of these melt polymers are in excess of 100% of theory and about 120%. Thus, they have high amounts of non-polymeric matter which is lost when they are heated to high temperatures. Also, the hydroxy polymer, DA-39-97, is most probably lower in molecular weight than the other two, because whereas the unsubstituted azine polymer, DA-39-45(a)-p, and the methoxy azine polymer, DA-39-99, are black in color, which is indicative of long range conjugation and high molecular weight, the hydroxy polymer was brown and apparently of lower molecular weight.

A comparison of these thermograms with those of the yellow polymers reveals that, with the exception of the hydroxy polymer, DA-39-97, the black polymers are more stable than the yellow polymers with respect to the temperature at which major weight losses occur. It should also be pointed out in this regard, that in the case of the black polymers, their elemental analysis for nitrogen indicates [N = 5.80% for DA-39=45(a); and N_2 = 5.85% for DA-39-97][9] that they have already lost a good portion of the nitrogen initially present because their syntheses are performed at temperatures in the range 200-300°C. In comparison, the yellow polymers, prepared in solution at relatively lower temperatures, have lost little if any of their nitrogen. It appears reasonable to say that the major weight losses for the yellow solution polymers are due mainly to decomposition, whereas those of the melt polymers are due primarily to low molecular weight oligomers resulting from chain-end coupling and to occluded unreacted monomers.

b. Thermal Stability of Black Polymers Recycled in Nitrogen.

The thermograms Appendix Nos. 33-2, 34-2, 35-2, 36-2 and the data of Table 13 show that once the nitrogen has been eliminated from the polymers, and chain-end coupling and other reactions have been completed in nitrogen, the derived polystilbene-type polymers suffer little weight-loss on reheating and are stable in nitrogen to at least 1176°C.

c. Thermal Stabilities in Air of Black Polymers Recycled in Nitrogen.

Thermograms 33-3, 34-3, 35-3, 36-3 and 38 and the data of Table 14 show that the polystilbene-type polymers derived from the black polyazines are more resistant to air oxidation than the black polyazine from which they were derived. The parent polyazine, DA-39-45(a)-p and the methoxy substituted polyazine, DA-39-99, show about the same stability in air up to about 590°C, whereas the hydroxy substituted polyazine, DA-39-97, is more stable extending to 650°C.

d. Thermal Stabilities in Air of Black Polymers, as Synthesized and Without Preheating in Nitrogen.

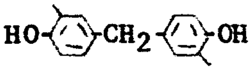
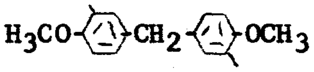
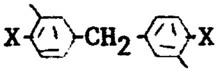
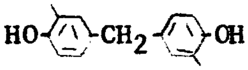
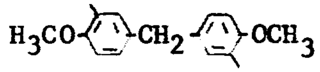
The data of Table 15 and thermograms Appendix Nos. 39, 40, 41, 42 and 43 show that these non-preheated polymers are less stable than those that have eliminated nitrogen by preheating in nitrogen.

The parent polymer, DA-39-45(a) and the hydroxy polymer, DA-39-97, show comparable thermal stability in air to about 450°C whereas the methoxy derivative shows a thermal stability in air to about 375°C.

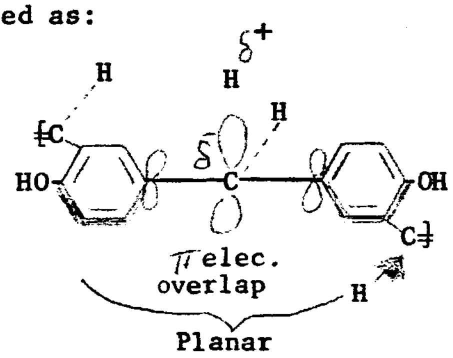
e. Effect of Particle Size on Thermal Stability Values.

The TGA determinations were performed on the black polymer, DA-39-45(a), in two different forms; one in the form of a fine powder, DA-39-45(a)-p, and the other in the form of a button or solid mass, DA-39-45(a)-m. The data in thermograms Appendix Nos. 33, 34, 37, 38, 39, 40 and 43 show that the massive form possessed a considerably greater thermal stability than the powdered form. This indicates that surface area is indeed a factor in these degradations and that the decomposition or combustion reactions take place primarily at the surface of the polymer. These reactions, in view of this evidence, can be considered more or less as diffusion-controlled.

<u>f. The Effect of the Aryl Moiety on Thermal Stability</u>.

While the above thermal studies compared yellow and black polymers, they also compared at the same time, the effect of the  moiety with the  and  moieties. In these studies which involved heating in nitrogen, recycling in nitrogen, heating the recycled polymer in air, and heating the as-synthesized polymer in air, no strict order of stability could be assigned to these moieties. What is important, is, that the order of magnitude of the stabilities of the  moiety and the  moieties, represented by  and  are comparable. The introduction of the aliphatic $-CH_2-$ linkage between the benzene rings in these moieties would be expected to reduce the thermal stability. The contrary result allows us to draw some conclusions about the nature of the spacial structure of the methylenedisalicylaldehyde nucleus in the polymer chain. It is conformationally impossible for the two phenyl rings substituted to the methylene group to be planar if we assume that the methylene group is tetragonal, as it normally is. It has also been well documented that conjugation enhances greatly the thermal stability of a polymer. Since the disalicylaldehyde polymers possess at least as much stability as the phenylene azine, they should possess therefore some good measure of conjugation.

It is known, however, that the phenylene polymers are fully conjugated and planar, therefore it can be assumed that the disalicylaldehyde polymers are also highly conjugated and planar. This means that the methylene group does not interrupt the effective conjugation and that it cannot be tetragonal. Therefore, it participates most probably in a form of hyperconjugation, one form of which is pictured as:

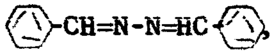


This effect has also been termed pseudoconjugation and is found in the poly-Schiff bases.[2,13]

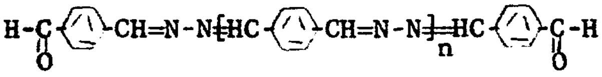
VI. Molecular Weight Determinations.

In dealing with polymers and polymer-related phenomena, it is always desirable to have some measure of the molecular weight of the polymer under study. To date, no method has been found suitable for the determination of the molecular weight of the black polyazine. Studies are planned utilizing the end group analysis method. The present studies have been limited to low molecular weight polymers; even though the unsubstituted yellow low molecular weight polymers are insoluble in solvents normally used for determining molecular weights through colligative properties. However, the low molecular weight methylene disalicylaldehyde azine polymer was found, because of the presence of the phenolic hydroxyl groups, to be soluble in concentrated aqueous alkali solutions. This permitted viscometric measurement which, with IR spectra and elemental analysis, enabled a molecular weight range to be determined.

A. Infrared Spectroscopy.

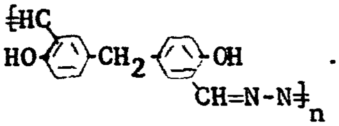
To determine the nature of the end-groups present in the yellow polymer, DA-39-34,  , an infrared spectrum was recorded of the polymer, Appendix No. 44, for comparison with the spectrum of the benzalazine monomer,  Appendix No. 45. It will be noted that both spectra are very similar, but that the polymer contains a sharp band at 5.93μ which is indicative of a carbonyl conjugated function; this band is not found in the benzalazine spectrum. Also there is no indication of (-NH_2) stretching frequencies in the polymer spectrum. Therefore, it can be concluded that the polymer does in fact contain only aldehyde end groups. Further, the strength and sharpness of the carbonyl band indicates that the carbonyl is relatively plentiful and that the $\overline{DP}$ of the polymer is not large.

B. Elemental Analysis.

With the knowledge that the yellow polymer DA-39-34 contains carbonyl end groups and is of low molecular weight, it should be possible to approximate the $\overline{DP}$ from the nitrogen content of the polymer determined by elemental analysis. This polymer was analyzed for nitrogen and was found to contain 17.15% nitrogen.[9] Assuming  as the basic structure, the DP of this polymer was calculated to be 3-4, that is, a mixture of n = 3 and n = 4 with a corresponding molecular weight of ~ 700.

C. Intrinsic Viscosity.

In order to achieve solubility in alkali the hydroxy functional group was incorporated into the yellow azine polymer, DA-39-93,



.

This polymer was used in 10% (~2.5 N) aqueous sodium hydroxide. The viscosities were measured in the usual way in a dilution viscometer and the intrinsic viscosity $[\eta]$ was determined graphically by plotting η_{sp}/conc. versus conc., and then extrapolating to conc. → 0, as shown in the plot of Appendix No. 46.

1. Experimental.

(DA-39-101) Viscosity Determinations of DA-39-93.

The polymer, 0.1042 g., was dissolved in 25 ml. of 10% aqueous sodium hydroxide and equilibrated in a constant temperature water bath at 30°C. Then a 3.0 ml. aliquot was then placed into a clean dry Cannon-Ubbelohde Semi-Micro Dilution Viscometer. After the polymer solution in the viscometer became thermally equilibrated, its flow time was measured to ± 0.01 sec. in triplicate. Sequential additions of solvent of 1, 2, 3, 4 ml. were then made to produce increasingly more dilute solutions. These each were thermally equilibrated and their flow time measured in triplicate. The solvent alone was also run through the viscometer in triplicate. The data is summarized in Table 16.

Table 16

Viscosity Data on Polymer DA-39-93

Conc. g/100	sec.	η/η_o	η_n	η_{sp}	η_{sp}/c
0.4168	368.1	368.1/358.1	1.028	0.028	0.0672
0.3126	365.3	365.3/358.1	1.020	0.020	0.0640
0.2084	362.4	362.4/358.1	1.012	0.012	0.0576
0.1563	361.0	361.0/358.1	1.008	0.008	0.0512
0.1042	360.0	360.0/358.1	1.005	0.005	0.0480

D. Discussion.

From the plot of η_{sp}/c vs c as c → 0 the intrinsic viscosity is determined $[\eta] = 0.042$ dl/g. The viscosity of this yellow polymer is very low and confirms the conclusion that its $\overline{DP}$ is also low; a conclusion which well applies to the other yellow polymers.

VII. Summary and Conclusions.

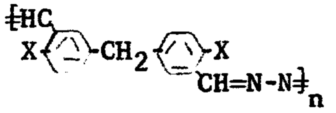
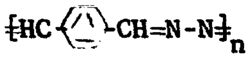
(1) Two monomers, 5,5'-methylene disalicylaldehyde and 5,5'-methylene dimethoxydisalicylaldehyde, were synthesized and then polymerized in solution with hydrazine. They produced infusible yellow brick-dust polymers. These monomers were also polymerized in the melt method to yield infusible high molecular weight black polymers.

(2) Thermoanalytical studies were employed to monitor the decomposition of the azine polymers which were shown to lose nitrogen and form a thermally stable polystilbene-type polymer upon heating. Thermal gravimetric analyses, differential thermal analyses and calorimetric data were all employed in the thermoanalytical studies.

(3) The method of Freeman and Carroll[8] was used in connection with a TGA thermogram to estimate the order of the decomposition reaction as well as its activation energy. It was determined to be essentially first order and $E_a = 24.7$ kcal/mole.

(4) The ΔH of this decomposition was estimated from calorimetric measurements. The similarity of the heat-treated azine polymers to graphite, when oxidized at temperatures $> 580°C$, was demonstrated.

(5) The thermal stabilities of both the yellow and the black azine polymers were determined by comparative TGA thermograms. It was shown that the black polymers are more thermally stable in nitrogen and air than the yellow polymers.

(6) Differences in the thermal stability of the methylene disalicylaldehyde nucleus,  $\overset{\{HC}{X\text{-}C_6H_3}\text{-}CH_2\text{-}\underset{CH=N\text{-}N\}_n}{C_6H_3\text{-}X}$ ($X = OH, OCH_3$), and the phenylene nucleus  $\{HC\text{-}C_6H_4\text{-}CH=N\text{-}N\}_n$ were shown to be negligible and evidence for hyper- or pseudo-conjugation of the methylene group was presented.

(7) The particle size of the polymers undergoing reaction in nitrogen and in air were shown to be important; the larger the particle the better the thermal stability. This indicated that many of the reactions may be diffusion controlled or proportional to the surface area.

(8) The effect of heating rate on the decomposition reactions was shown to be negligible.

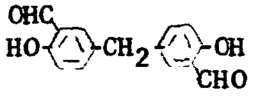
(9) An estimation of the molecular weight of the yellow polymers was made by examining infrared, elemental analysis and viscometric data. The IR indicated aldehyde end groups, while the elemental analysis suggested a $\overline{DP}$ of 3-4 and average molecular weight of 700.

(10) Polystilbene type polymers derived by heating the polyazines in nitrogen to 1176°C are stable in nitrogen to 1176°C.

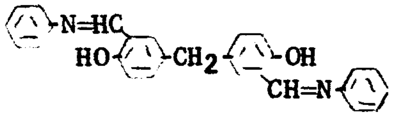
(11) Polystilbene-type polymers which have been heated in nitrogen to 1176°C show stabilities in air of at least 590°C. The highest one shows a value of about 650°C.

VIII. Glossary.

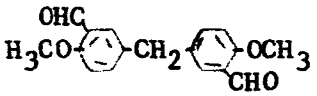
1. MDS =



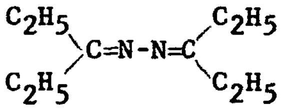
2. MDSDA =



3. MDMS =

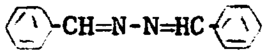


4. D-3-PA =



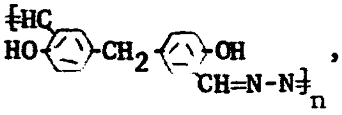
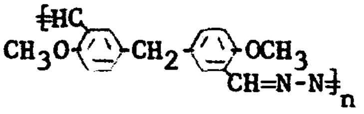
$(C_2H_5)_2C{=}N{-}N{=}C(C_2H_5)_2$

5. DBA =

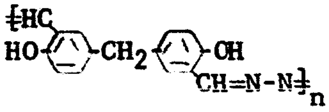


IX. Future Studies

(1) Complete the kinetic studies of the yellow polymers DA-39-93,


, and DA-39-95,  .

(2) Study the products of decomposition of the yellow polymers by mass spectral and other data.

(3) Employ titrimetric methods in examining the hydroxy substituted polyazine, (DA-39-93),  .

(4) Study the thermal reaction processes of the black melt polymers.

(5) Attempt to determine the molecular weight of the black melt polymers by end group analysis using especially the perfluoro drivatives, $F_5C_6N{=}HC-C_6H_4CH{=}NC_6F_5$ and $F_5C_6CH{=}N-N{=}HCC_6F_5$.

(6) Arrive at a consistent mechanism for the decomposition and oxidation reactions which is in agreement with all available data.

(7) Determine the effects, if any, on the properties of the melt polymers by varying the polymerization parameters.

X. Bibliography.

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2. 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.
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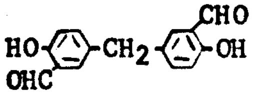
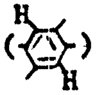
XI. Acknowledgment.

The authors and the University of Notre Dame gratefully acknowledge 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.

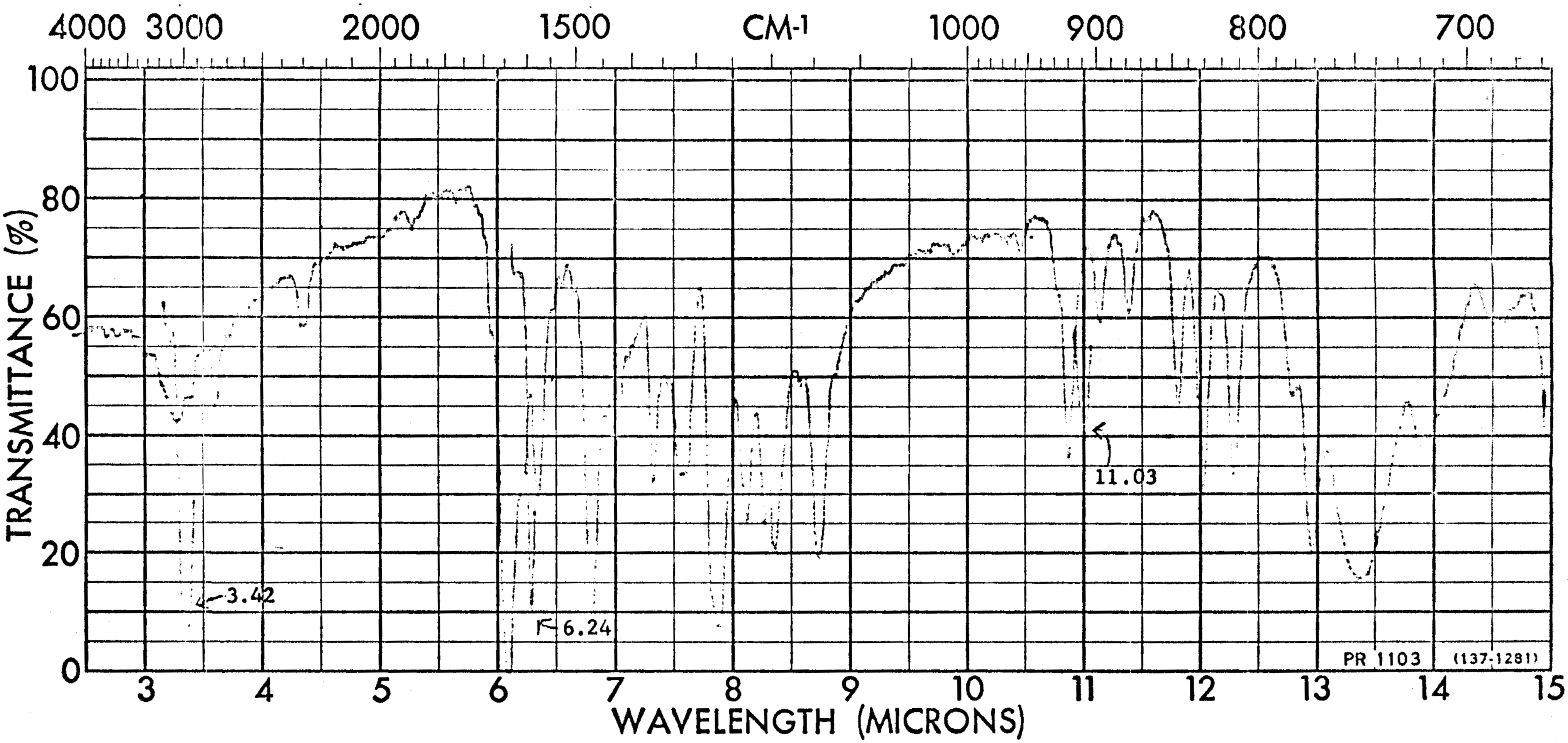
Appendix No. 1

NMR of DA-39-82 

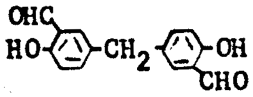
Std. TMS

cps	# protons	Assignment
230.2	2	$-CH_2-$
430	8	(-OH), ()
505.7	2	-CHO

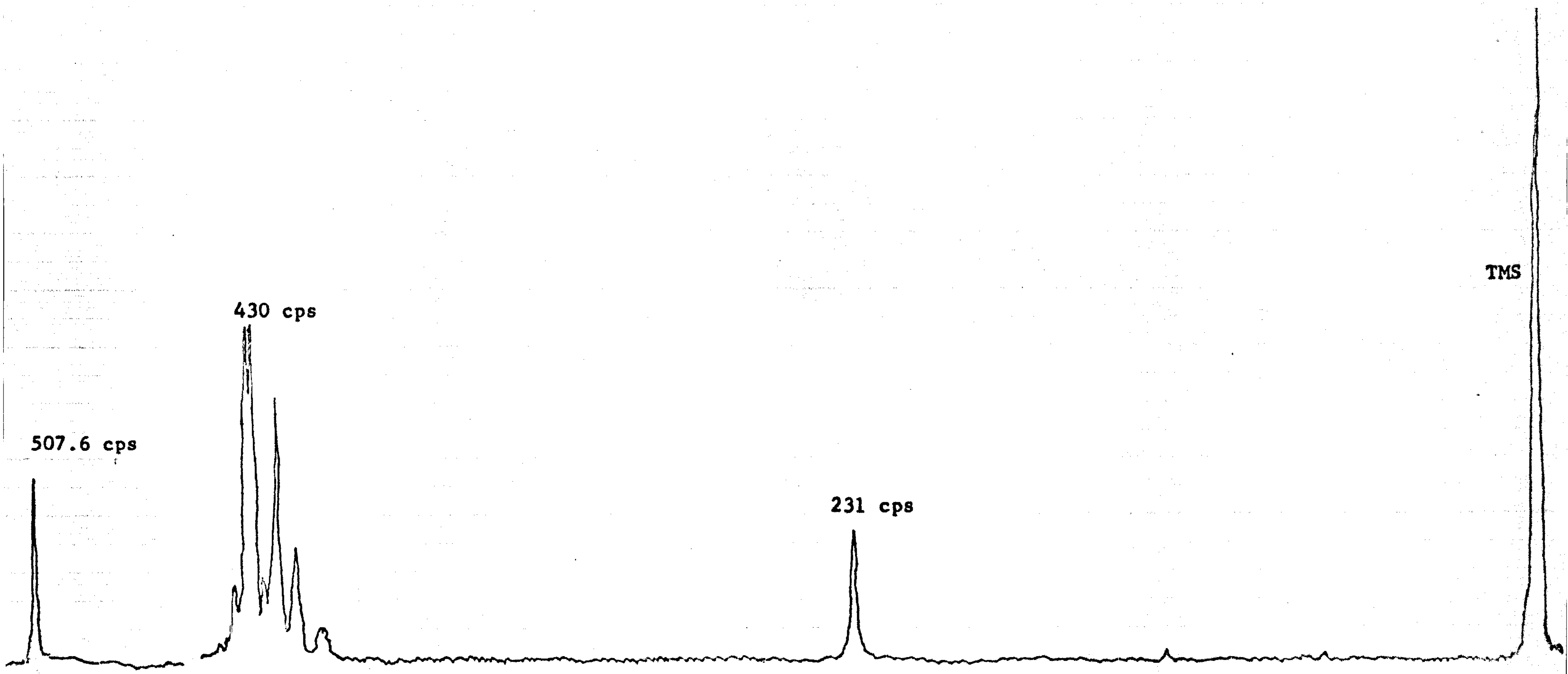
Appendix No. 2



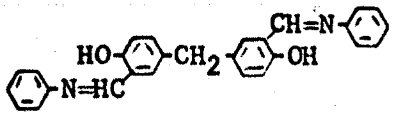
IR of DA-39-82



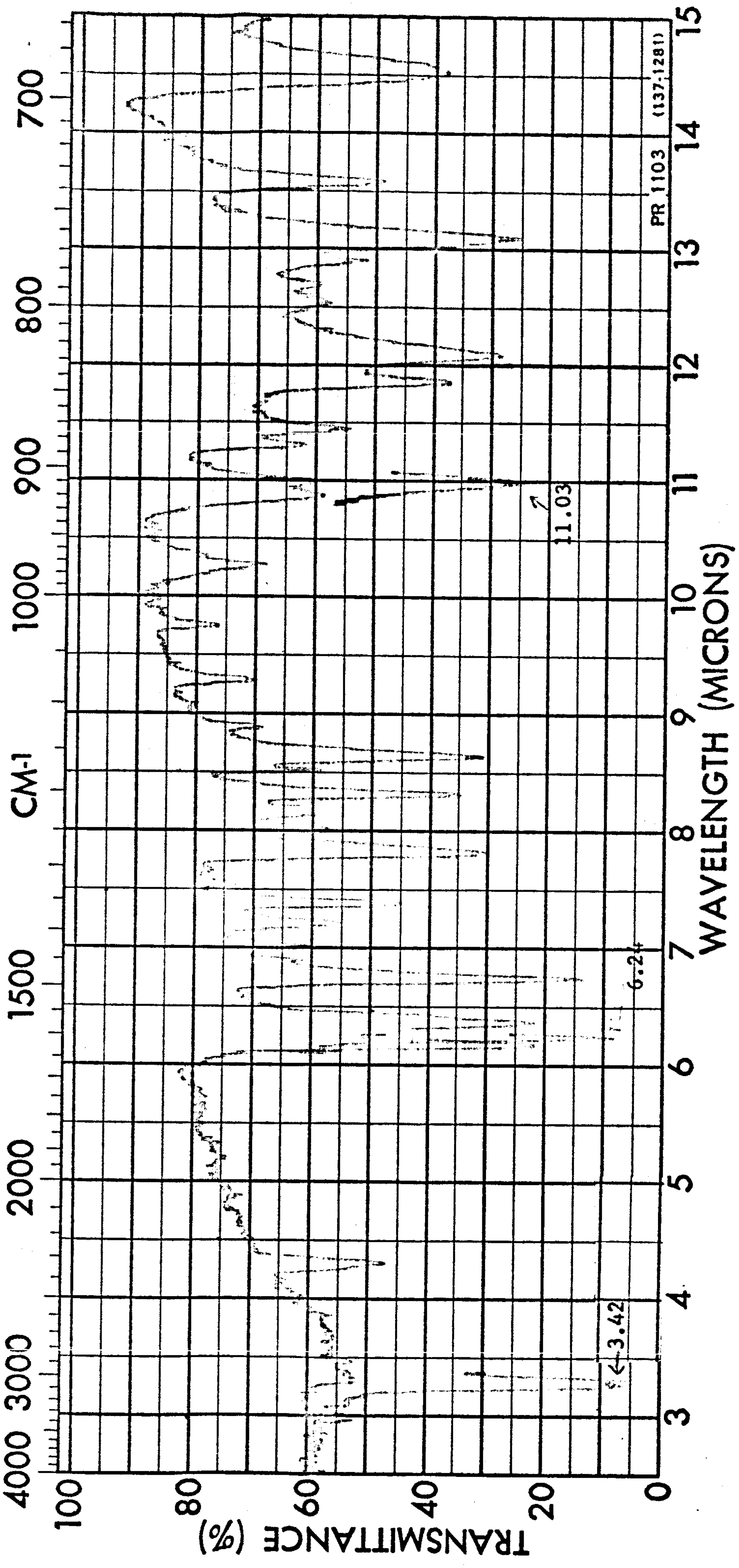
KBr Pellet 10-30-65



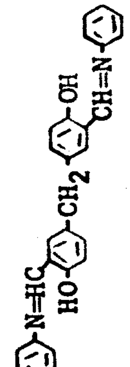
NMR of DA-39-83



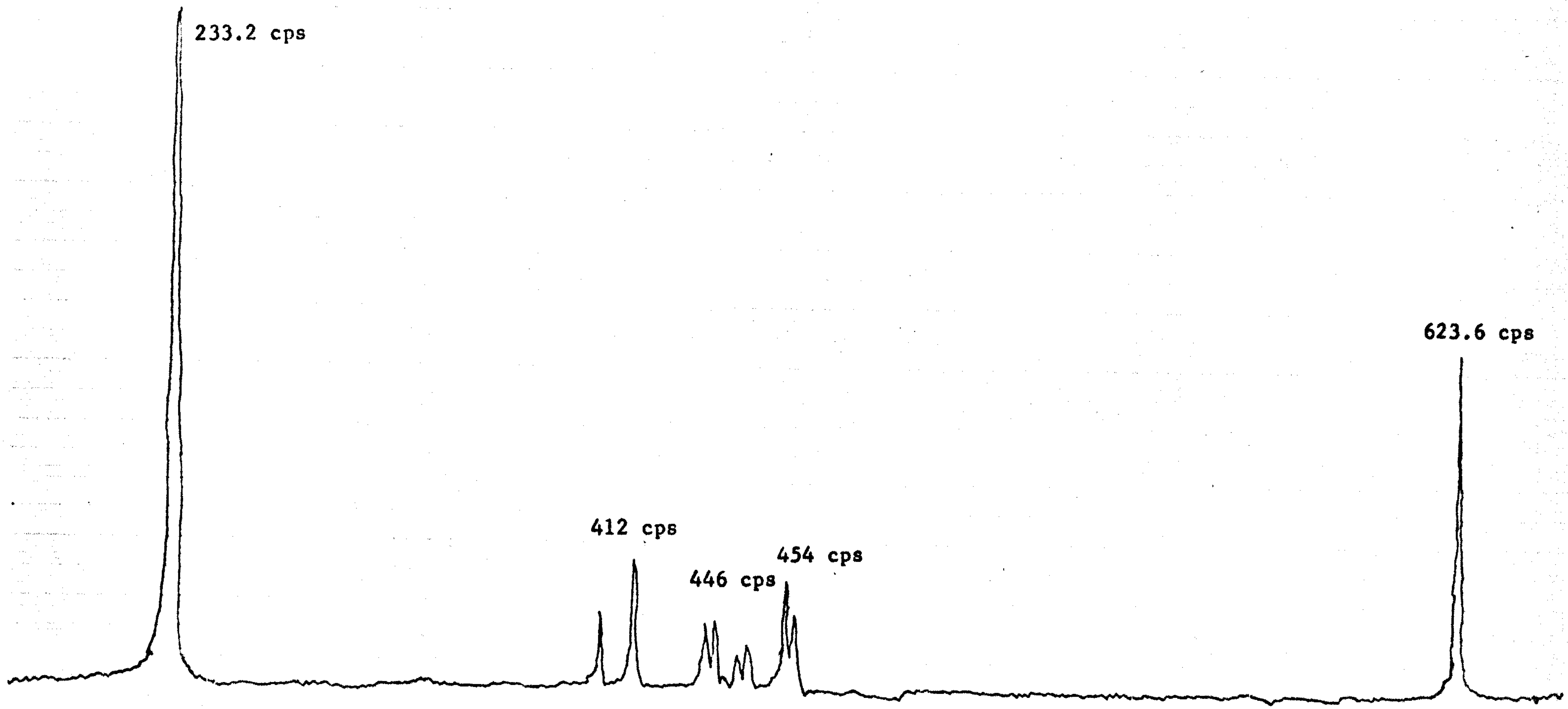
Std. TMS	cps	# protons	Assignment
	231.0	2	$-CH_2-$
	430	18	(-OH) and Ar-H
	507.6	2	-CH=N-



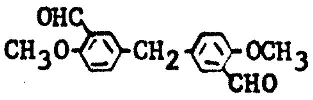
IR of DA-39-83



KBr Pellet 11-4-65

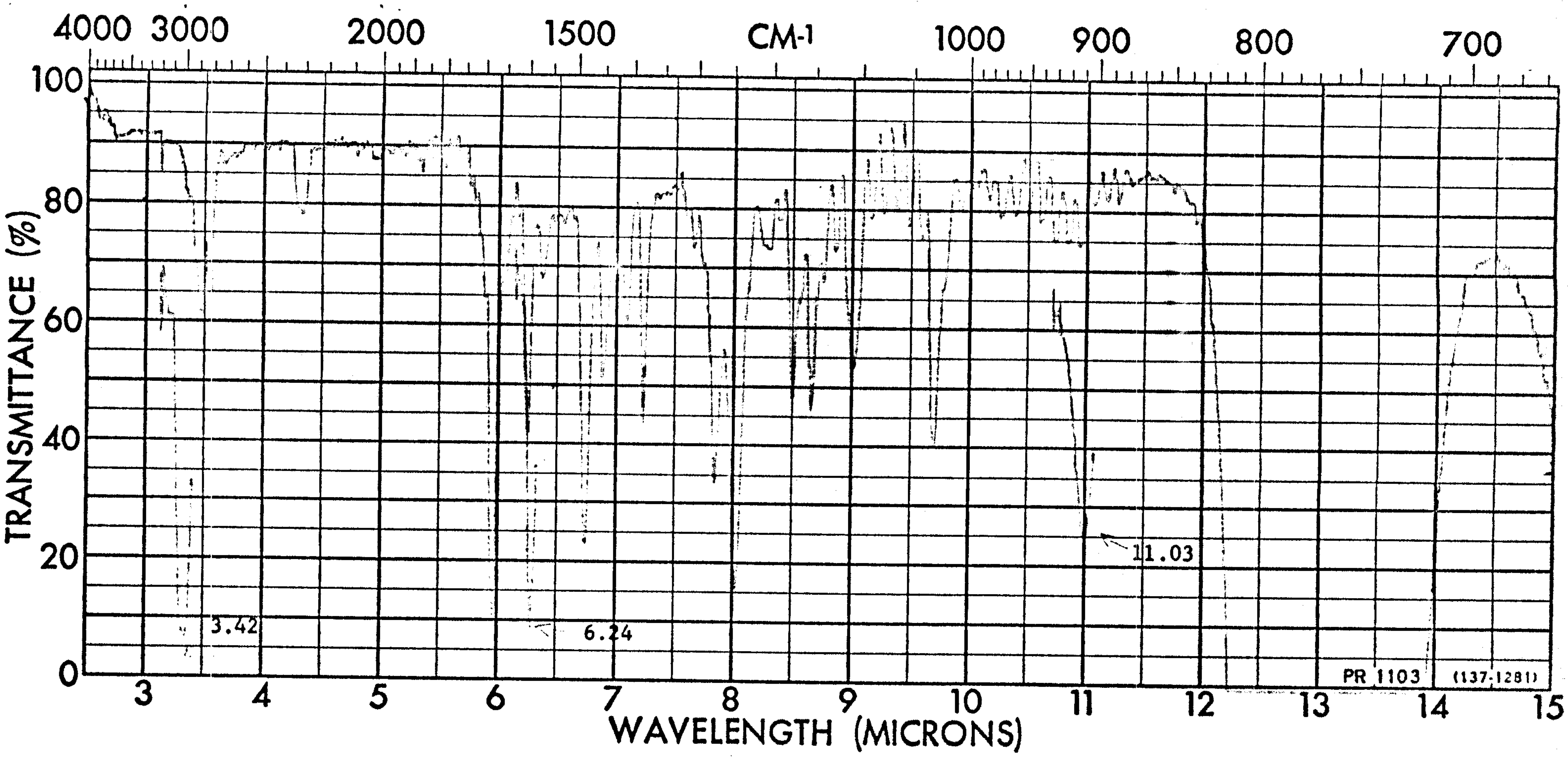


NMR of DA-39-89

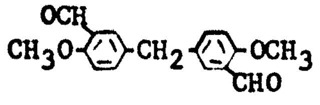


Std. TMS	cps	# protons	Assignment
	233.2	8	(-OCH$_3$-) (-CH$_2$-)
	412-460	6	Ar-H
	623.6	2	CHO

Appendix No. 6

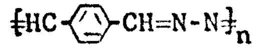


IR of DA-39-89



CCl_4 Solution 11-20-65

INSTRUMENT PRODUCTS DIVISION

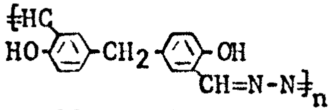
SAMPLE: DA-39-34	**X-AXIS**	**Y-AXIS**	RUN NO. ____ DATE 1-21-66
	TEMP. SCALE 50 °C/inch	SCALE 1 mg./inch	OPERATOR RKS
yellow polymer	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 5 °C/min.
			ATM. nitrogen
SIZE 11.06 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 5.06 mg.	TIME CONSTANT 2 sec.

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

Appendix No. 7

DU PONT INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

SAMPLE: DA-39-93



yellow polymer

SIZE 11.11 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

SCALE 1 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 5.11 mg.

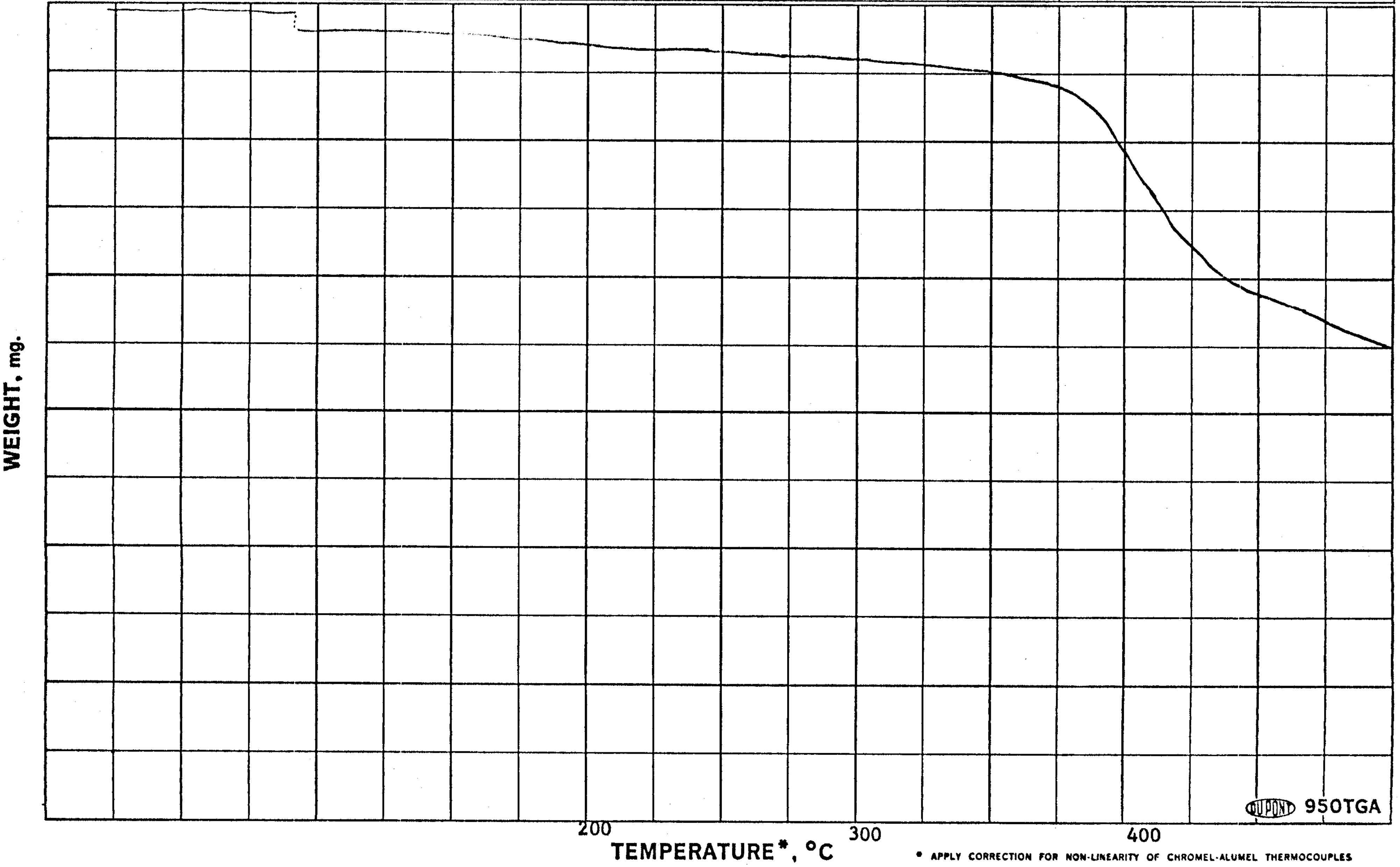
RUN NO. DATE 1-28-66

OPERATOR RKS

HEATING RATE 5 °C/min.

ATM. nitrogen

TIME CONSTANT 2 sec.

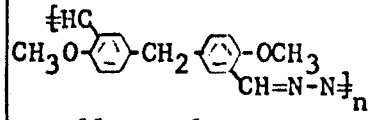


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 8

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

SAMPLE: DA-39-95



yellow polymer
SIZE 11.14 mg.

X-AXIS

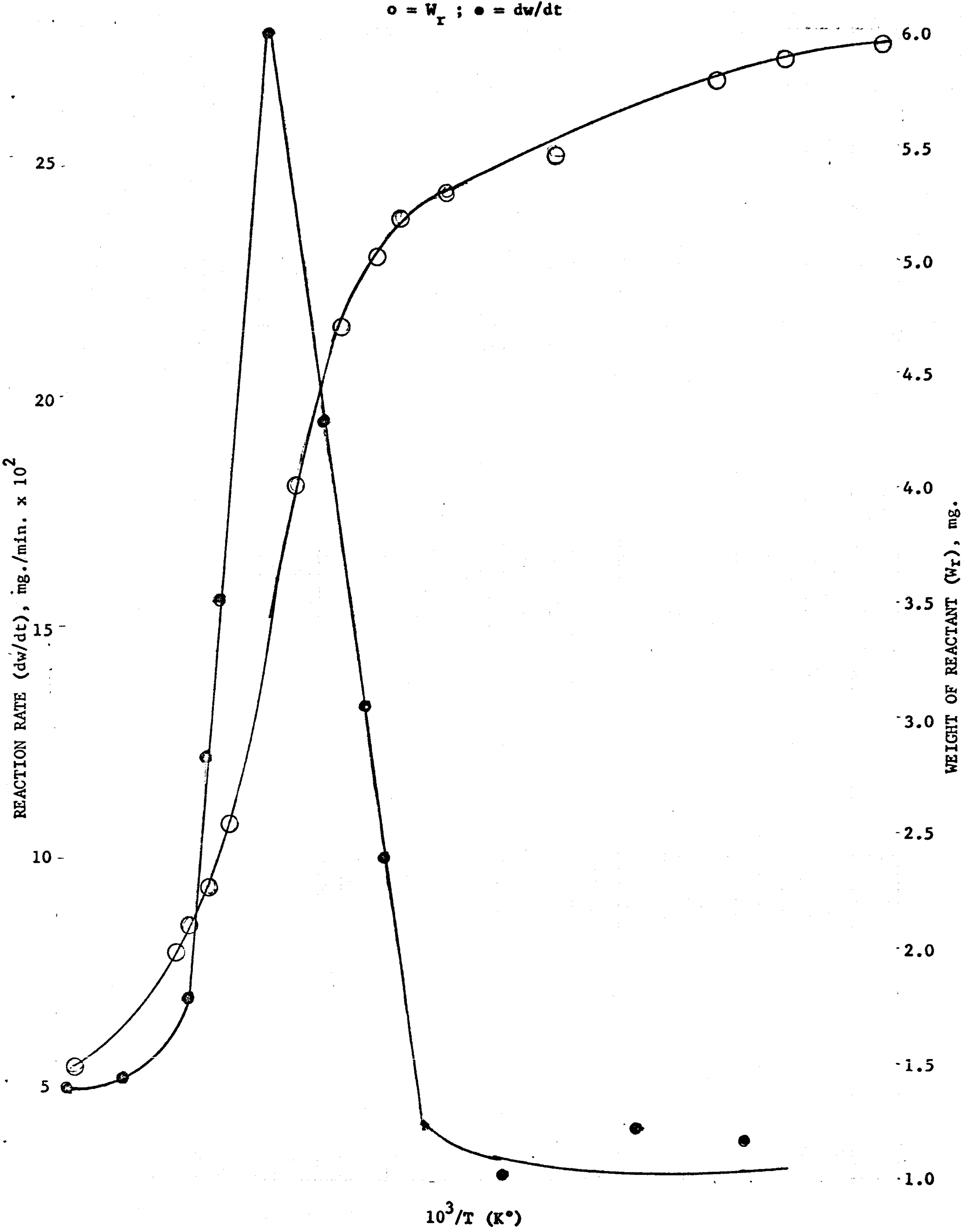
TEMP. SCALE 50 °C/inch
SHIFT 0 inch
TIME SCALE (ALT.) 0

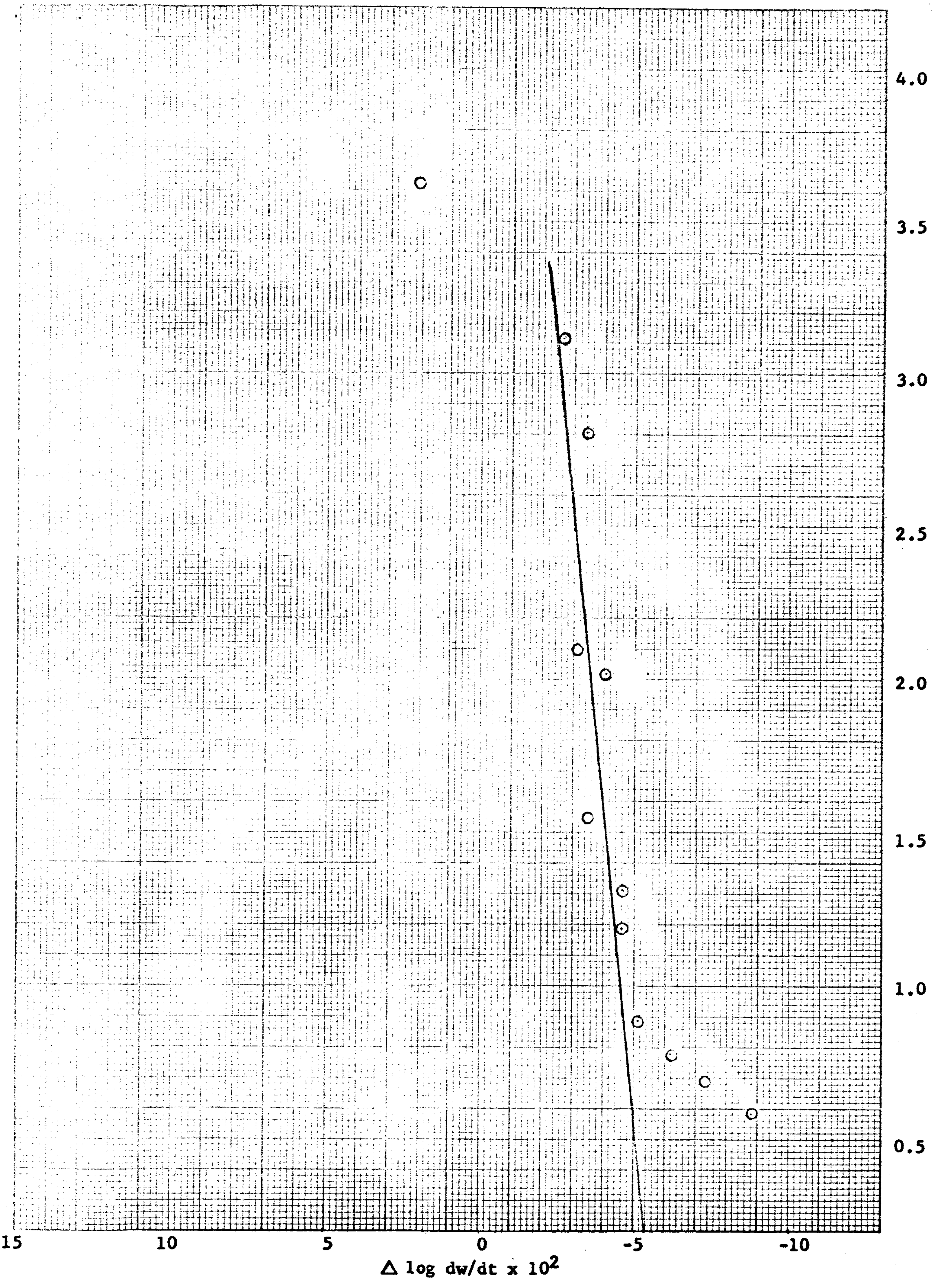
Y-AXIS

SCALE 1 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 5.14 mg.

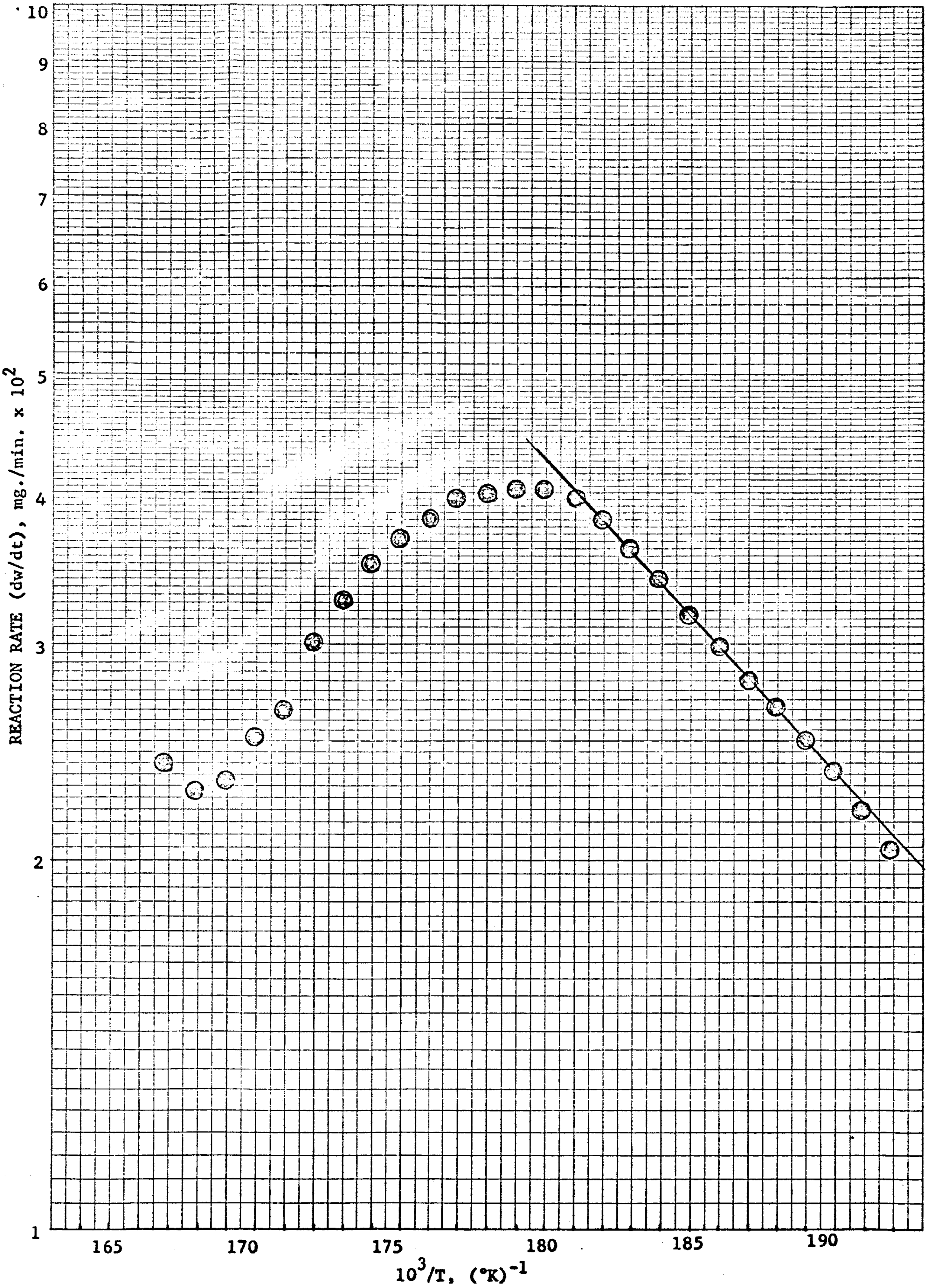
RUN NO. ____ DATE 1-28-66
OPERATOR RKS
HEATING RATE 5 °C/min.
ATM. nitrogen
TIME CONSTANT 2 sec.

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


o = W_r ; ● = dw/dt
REACTION RATE (dw/dt), mg./min. x 10^2
25
20
15
10
5
WEIGHT OF REACTANT (W_r), mg.
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
10^3/T (K°)


4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Δ log WT x 10^2
15
10
5
0
-5
-10
Δ log dw/dt x 10^2

Graph #3


10
9
8
7
6
5
4
3
2
1
REACTION RATE (dw/dt), mg./min. x 10^2
165
170
175
180
185
190
$10^3/T$, (°K)$^{-1}$

Appendix No. 13

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

SAMPLE: DA-39-34

yellow polymer

ORIGIN:

SIZE 3 mm.

REF. graphite

PROG. MODE heat

RATE 15 °C/MIN. START 25 °C.

ATM. A-N_2, B-N_2, C-air, D-air 760 MM

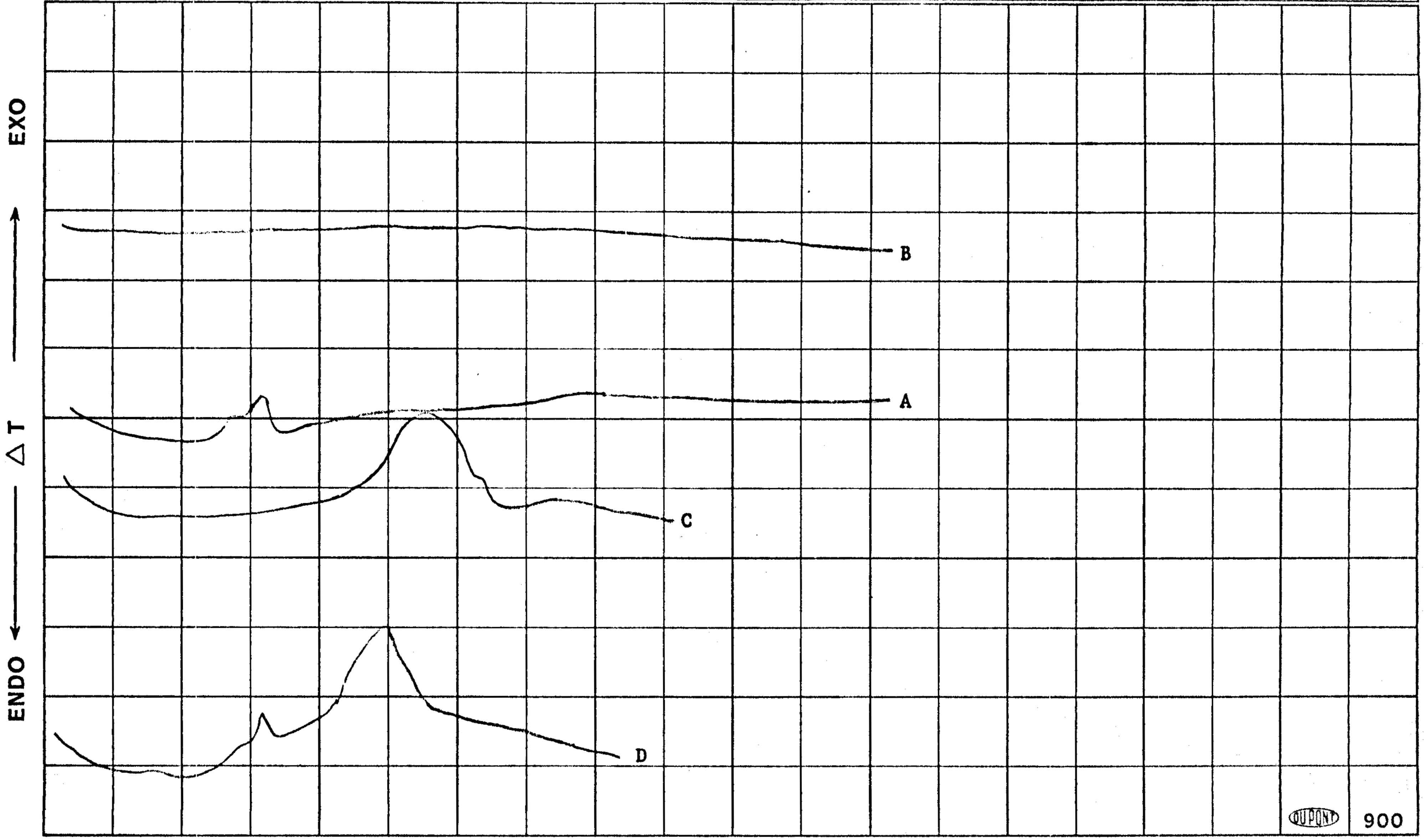
	T	△ T
SCALE	2 MV/IN.	0.04 MV/IN.
SHIFT	0 IN.	0 IN.

RUN NO.

DATE 11-24-65

OPERATOR RKS

BASE LINE SLOPE 0



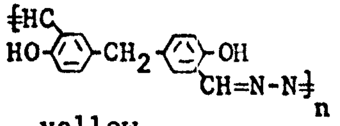
T (MILLIVOLTS; THERMOCOUPLE, REF. JUNCT. °C)

SAMPLE:

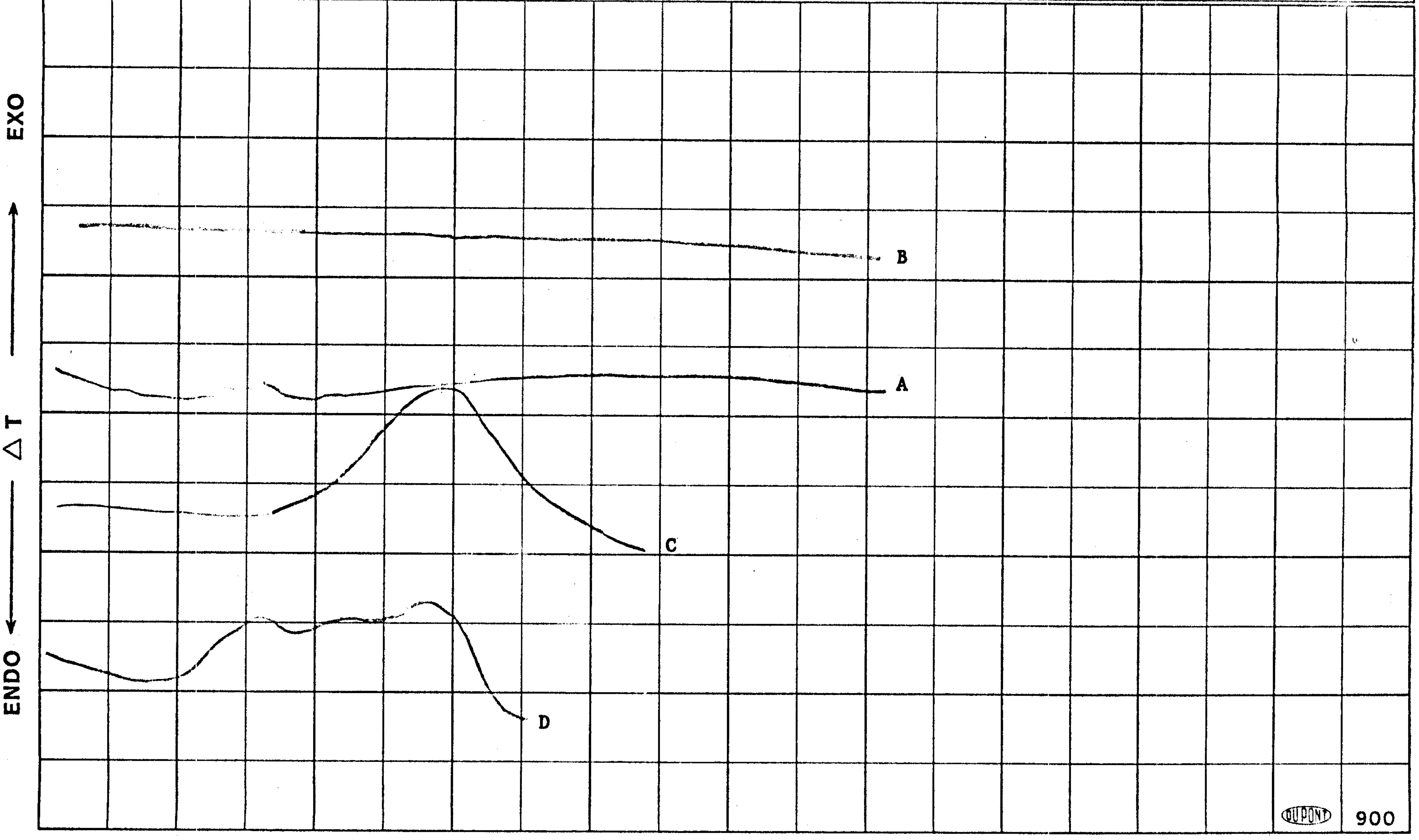
RUN NO.:

INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98 DELAWARE

SAMPLE: DA-39-93	SIZE 3 mm.	ATM. A-N_2, C-air; B-N_2, D-air	760 MM		RUN NO.
	REF. graphite		T	△ T	DATE 11-28-65
	PROG. MODE heat	SCALE	2 MV/IN.	0.04 MV/IN.	OPERATOR RKS
ORIGIN:	RATE 15 °C/MIN. START 25 °C.	SHIFT	0 IN.	0 IN.	BASE LINE SLOPE 0



yellow



T (MILLIVOLTS: THERMOCOUPLE, REF. JUNCT. °C)

SAMPLE: RUN NO.:

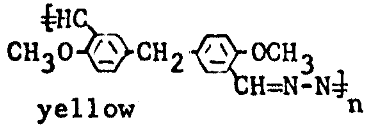
Appendix No. 14

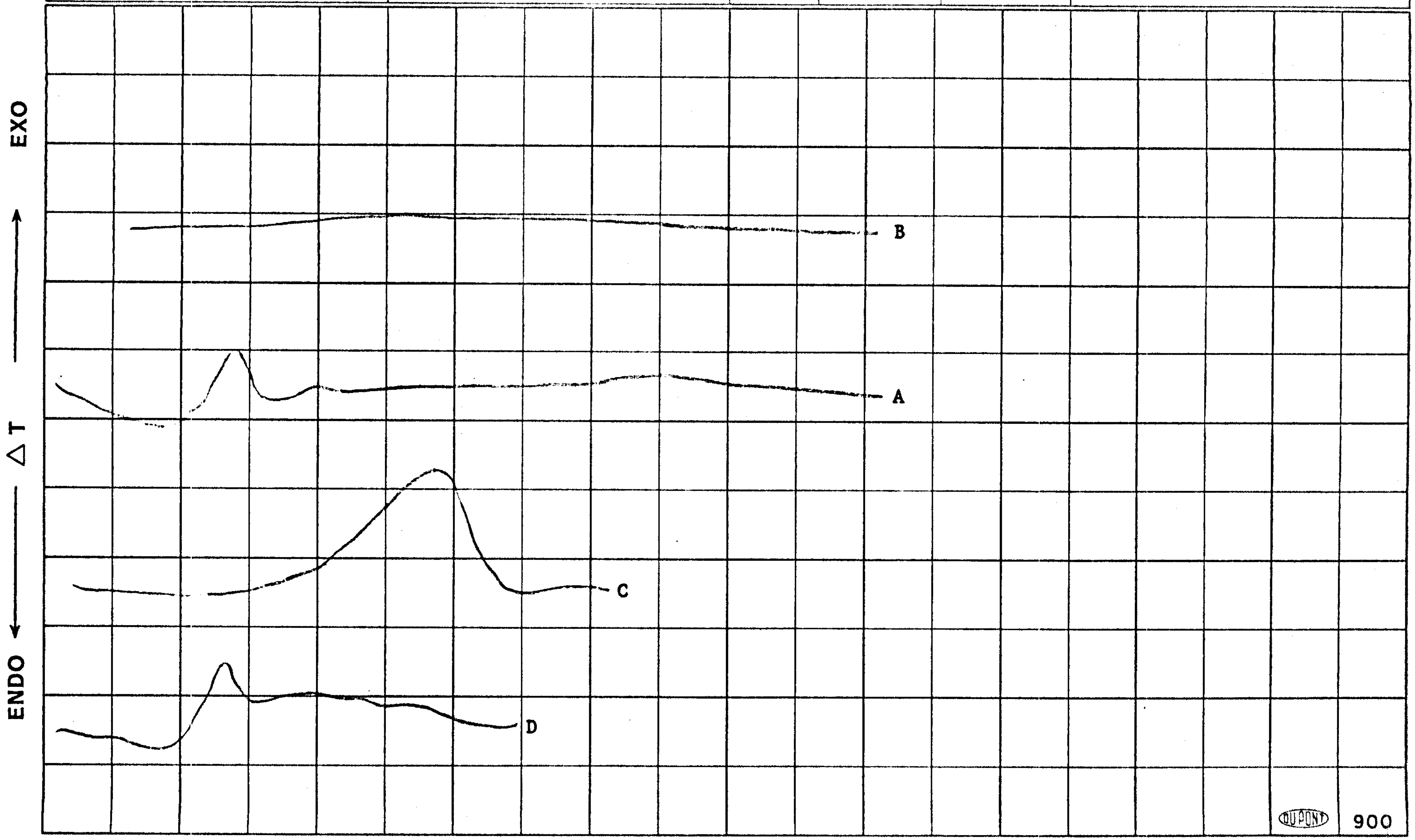
Appendix No. 15

SAMPLE:______ RUN NO.:______

DUPONT | INSTRUMENT PRODUCTS D: WILMINGTON 98 DELAWARE

SAMPLE: DA-39-95	SIZE 3 mm.	ATM. A-N_2, C-air B-N_2, D-air 760 MM	RUN NO.
	REF. graphite	T / △ T	DATE 11-30-65
yellow	PROG. MODE heat	SCALE 2 MV/IN. / 0.04 MV/IN.	OPERATOR RKS
ORIGIN:	RATE 15 °C/MIN., START 25 °C.	SHIFT 0 IN. / 0 IN.	BASE LINE SLOPE 0

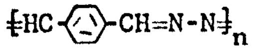




T (MILLIVOLTS;______ THERMOCOUPLE, REF. JUNCT.______ °C)

Appendix No. 16

SAMPLE: DA-39-34



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

yellow polymer

ORIGIN:

SIZE 7.37 mg.

REF. none

PROGRAM MODE heat

RATE 10 °C/MIN, **START** 25 °C

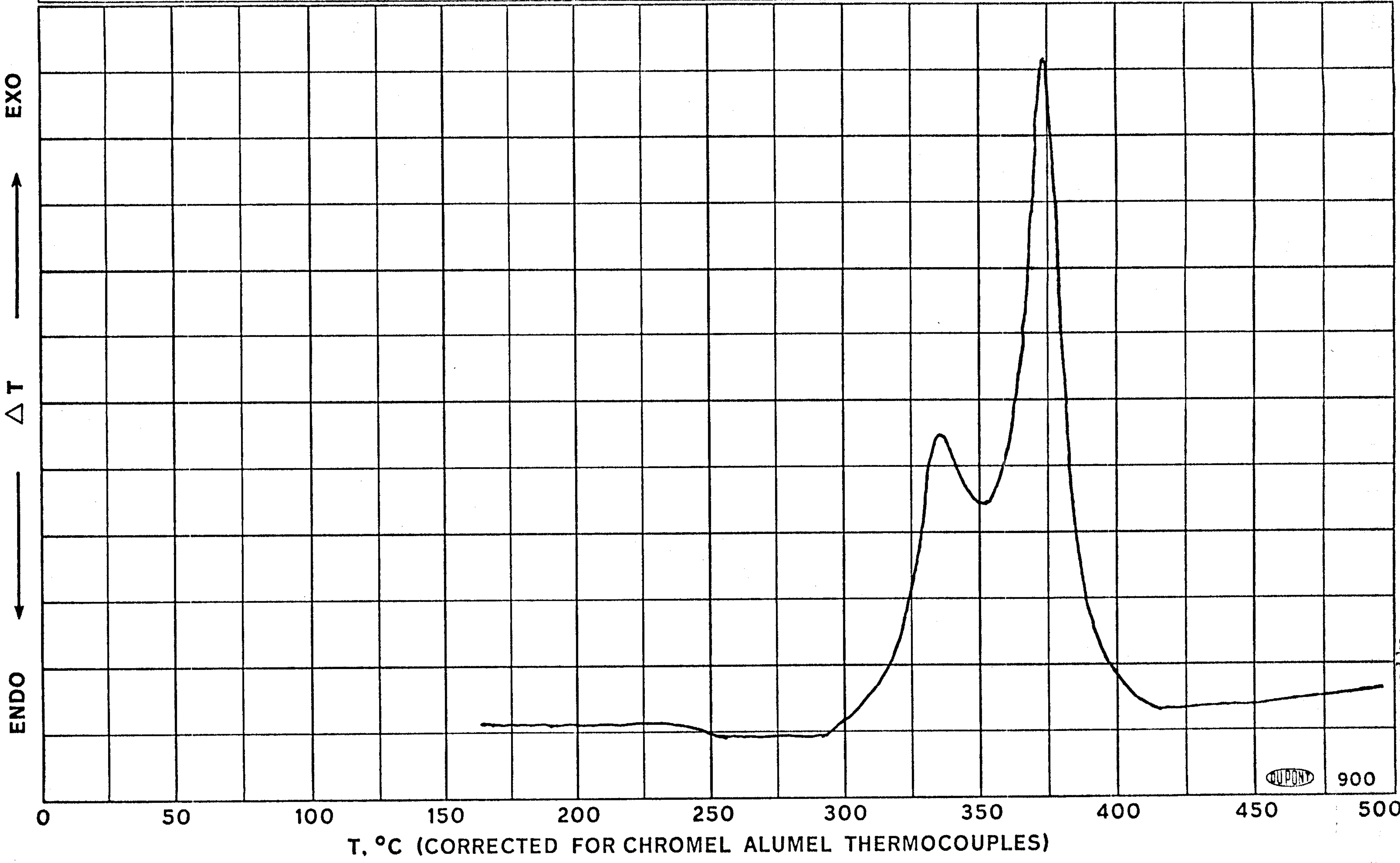
ATM. nitrogen 760

	T	ΔT
SCALE SETTING	50 °C/IN.	1 °C/IN.

RUN NO.

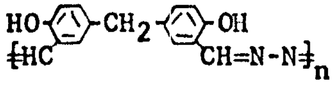
DATE 1-12-66

OPERATOR RKS



Appendix No. 17

SAMPLE: DA-39-93



yellow polymer

ORIGIN:

SIZE 7.86 mg.

REF. none

PROGRAM MODE heat

RATE 10 °C/MIN, START 25 °C

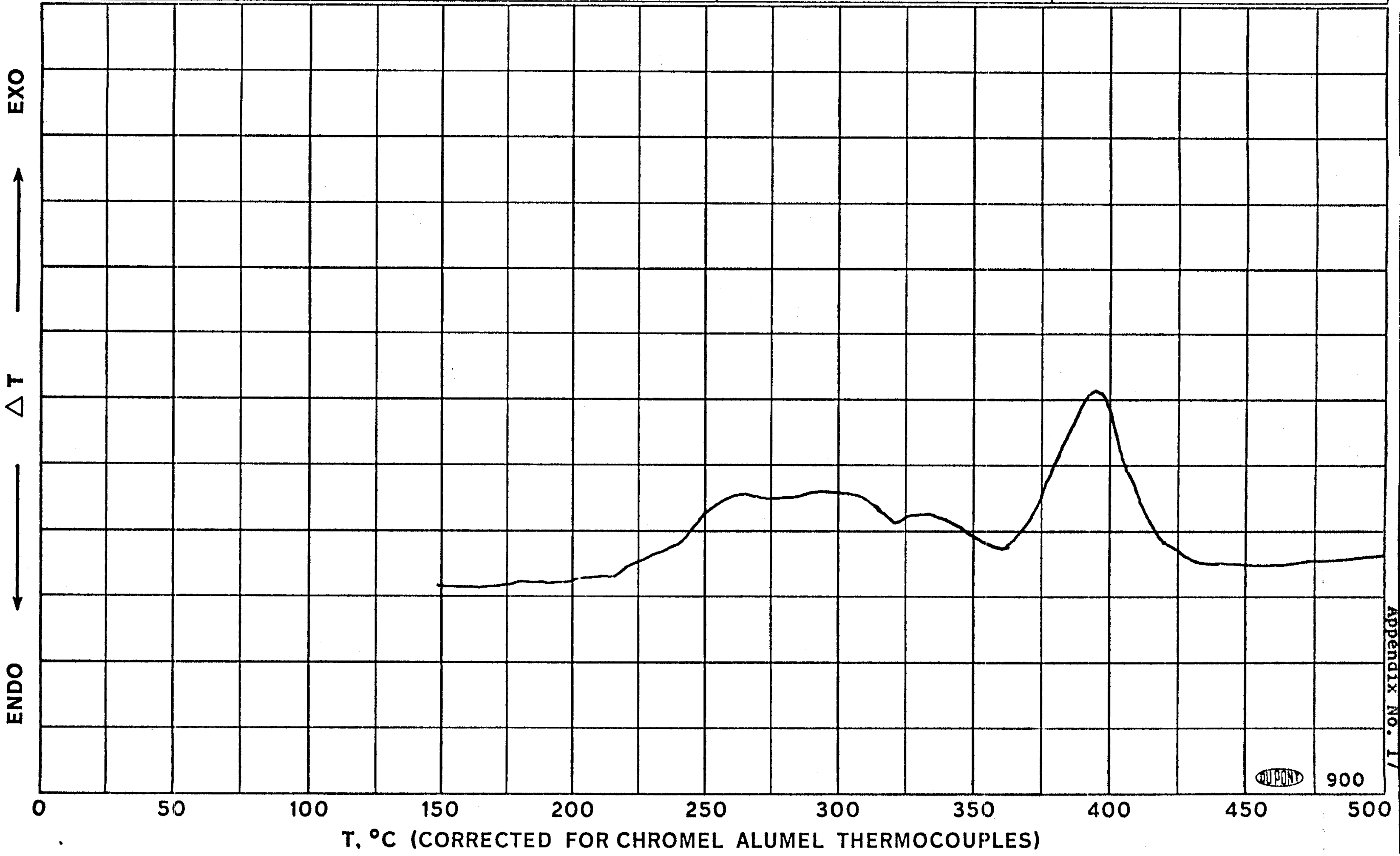
ATM. nitrogen 760

	T	△ T.
SCALE SETTING	50 °C/IN.	1 °C/IN.

RUN NO.

DATE 1-12-66

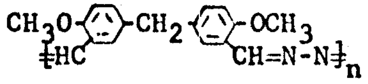
OPERATOR RKS



Appendix No. 18

SAMPLE: ______ RUN NO.: ______

SAMPLE: DA-39-95

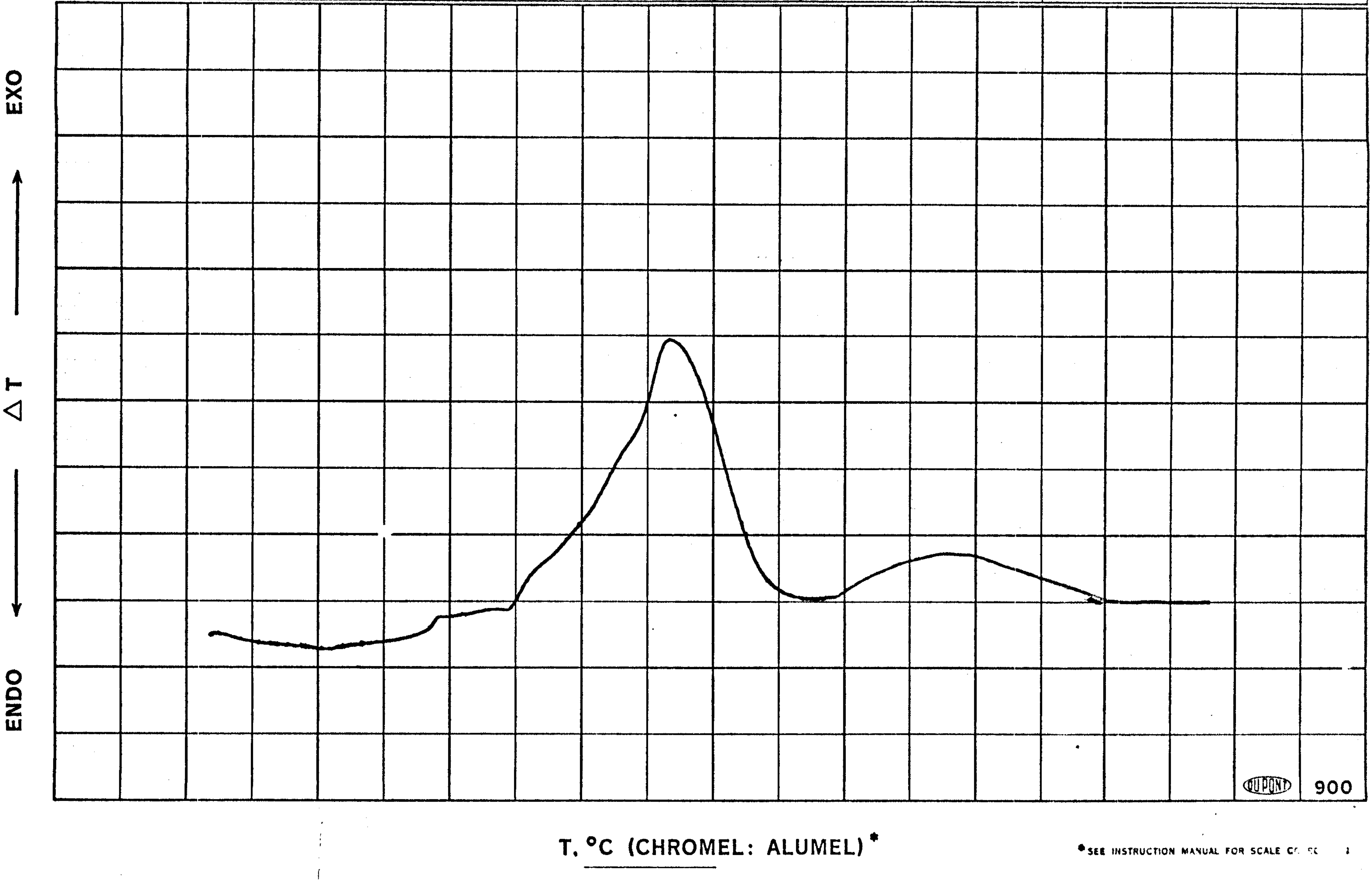


$CH_3O-C_6H_3(-CH=)-CH_2-C_6H_3(-OCH_3)-CH=N-N-]_n$

yellow polymer

ORIGIN:

SIZE 5.71 mg.	**ATM.** nitrogen, 760 **MM**			**RUN NO.**
REF. none		**T**	**△ T**	**DATE** 1-12-66
PROG. MODE heat	**SCALE**	50 °C/IN.	1 °C/IN.	**OPERATOR** RKS
RATE 10 °C/MIN **, START** 25 **°C**	**SHIFT**	0 **IN.**	0 **IN.**	**BASE LINE SLOPE** 0



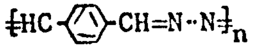
*SEE INSTRUCTION MANUAL FOR SCALE C

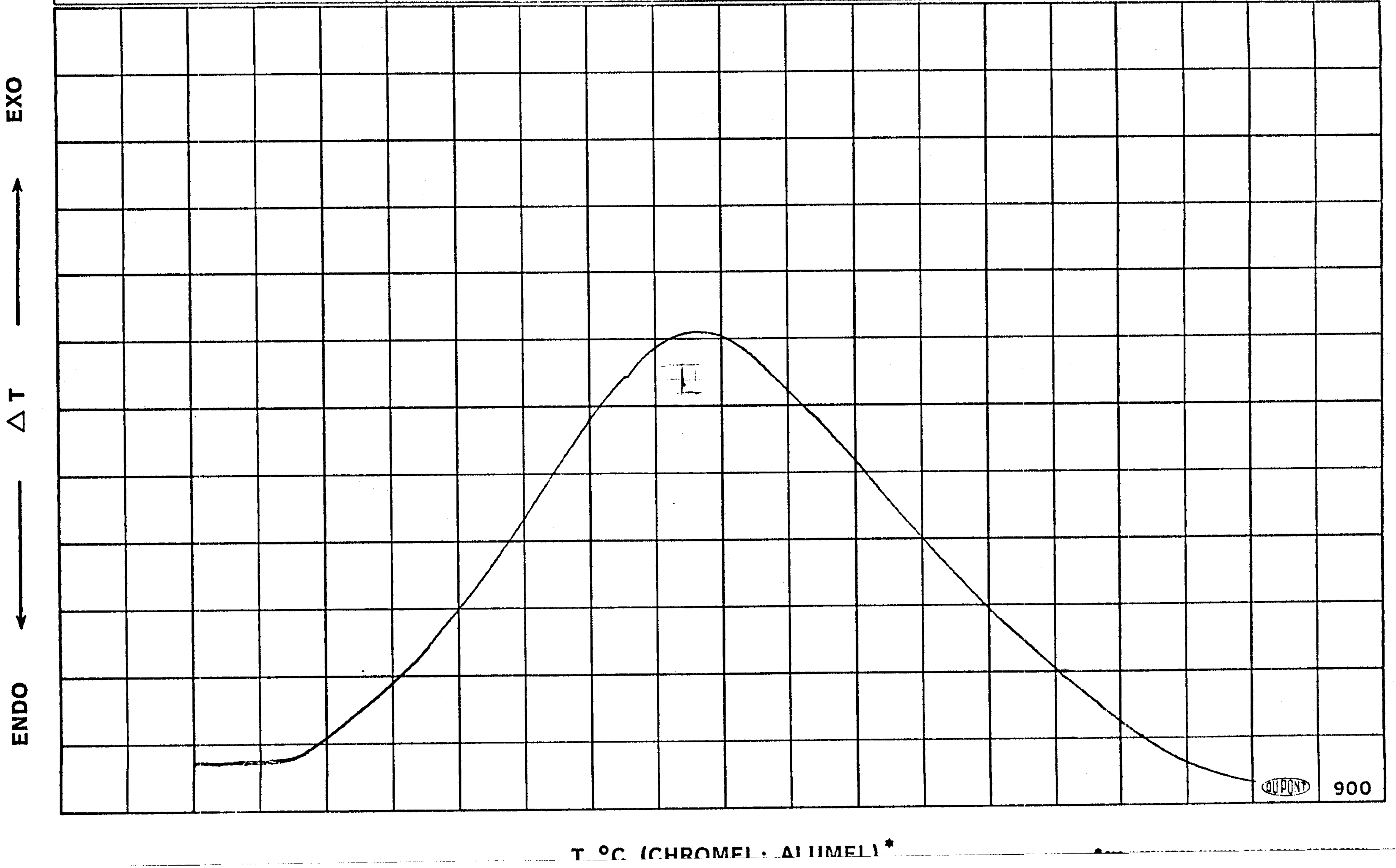
Appendix No. 19

SAMPLE:

RUN NO.:

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

SAMPLE: DA-39-94-1176	SIZE 4.72 mg	ATM. air, 760 MM		RUN NO.
 $\{HC-C_6H_4-CH=N-N\}_n$	REF. none	T	ΔT	DATE 1-19-66
yellow polymer	PROG. MODE heat	SCALE 50 °C/IN.	1 °C/IN.	OPERATOR RKS
Heated twice in N_2 to 1176°C ORIGIN:	RATE 10 °C/MIN, START 25 °C	SHIFT 0 IN.	0 IN.	BASE LINE SLOPE 0

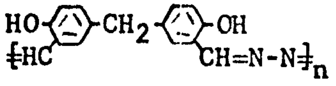


Appendix No. 20

SAMPLE: ____ RUN NO.: ____

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

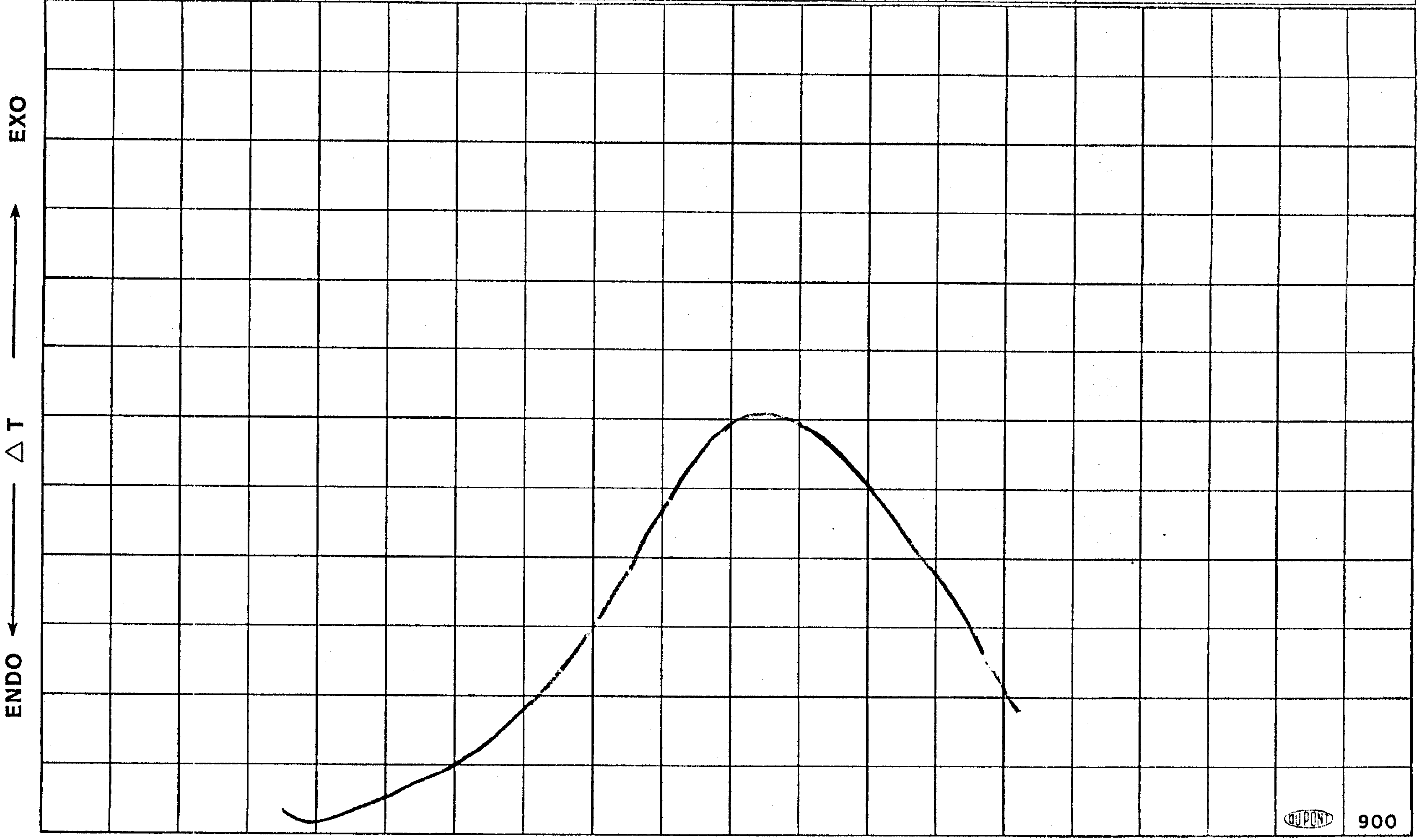
SAMPLE: DA-39-93-1176



yellow polymer
Heated twice in N_2 to 1176°C

ORIGIN:

SIZE 7.03 mg	ATM. air, 760 MM			RUN NO.
REF. none		T	△ T	DATE 1-19-66
PROG. MODE heat	SCALE	4 MV/IN.	0.04 MV/IN.	OPERATOR RKS
RATE 10 °C/MIN., START 25°C.	SHIFT	0 IN.	0 IN.	BASE LINE SLOPE 0



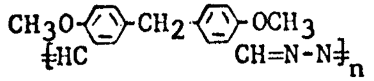
T (MILLIVOLTS: ____ THERMOCOUPLE. REF. JUNCT. ____ °C)

Appendix No. 21

SAMPLE:________ RUN NO.:________

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

SAMPLE: DA-39-95-1176



$CH_3O-C_6H_4-CH_2-C_6H_3(OCH_3)-CH=N-N\!\!+_n$ (ǂHC)

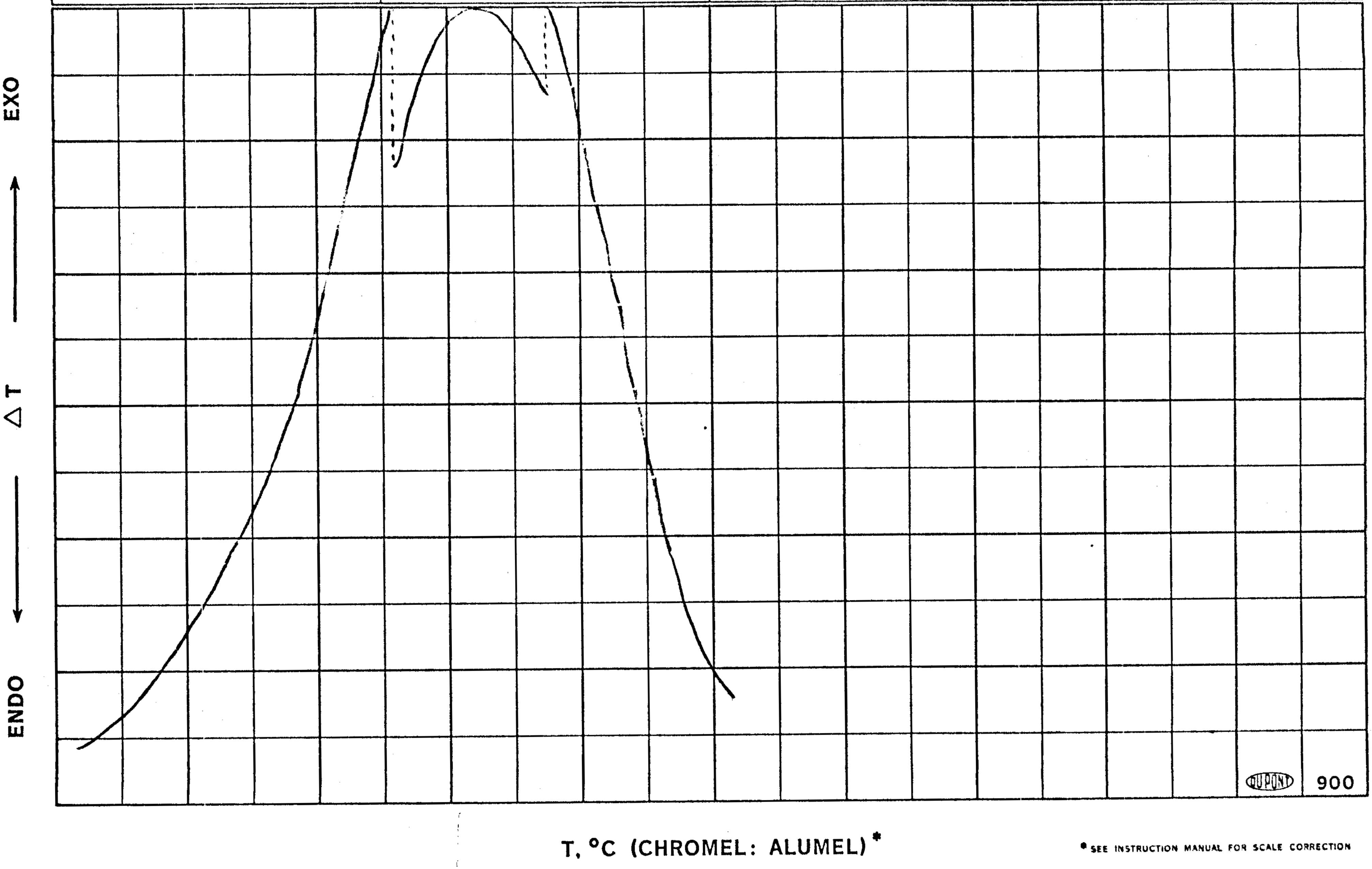
yellow polymer
Heated twice in N_2 to 1176°C
ORIGIN:

SIZE 7.87 mg.
REF. none
PROG. MODE heat
RATE 10 °C/MIN, START 25 °C

ATM. air, 760 MM

	T	ΔT
SCALE	100 °C/IN.	1 °C/IN.
SHIFT	0 IN.	0 IN.

RUN NO.
DATE 1-19-66
OPERATOR RKS
BASE LINE SLOPE 0

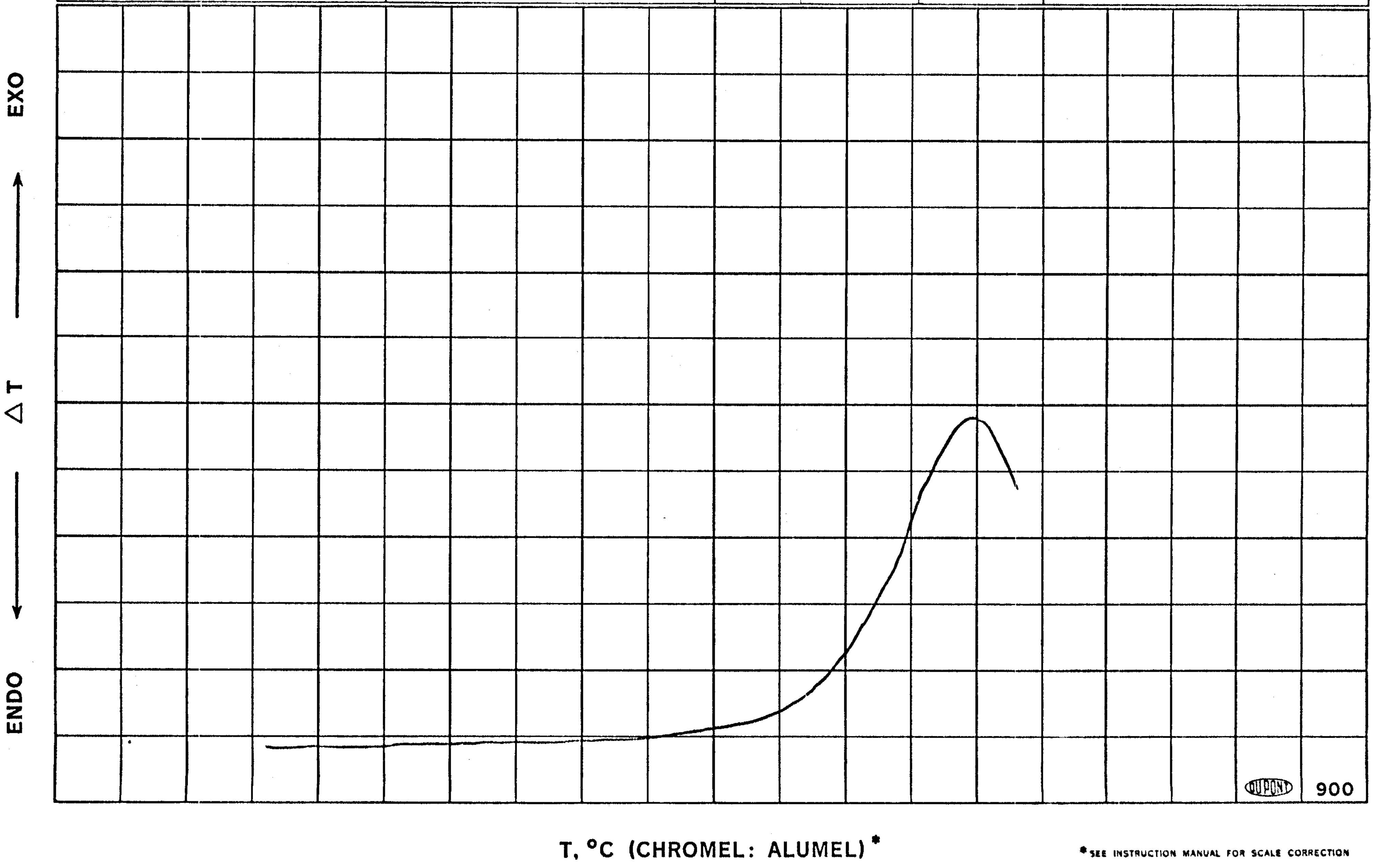


* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

Appendic No. 22

INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

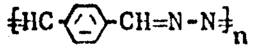
SAMPLE: Pyrolytic graphite	SIZE 6.84 mg.	ATM. air , 760 MM			RUN NO.
	REF. none		T	△ T	DATE 1-23-66
	PROG. MODE heat	SCALE	100 °C/IN.	1 °C/IN.	OPERATOR RKS
ORIGIN: NASA	RATE 10 °C/MIN, START 25 °C	SHIFT	0 IN.	0 IN.	BASE LINE SLOPE 0

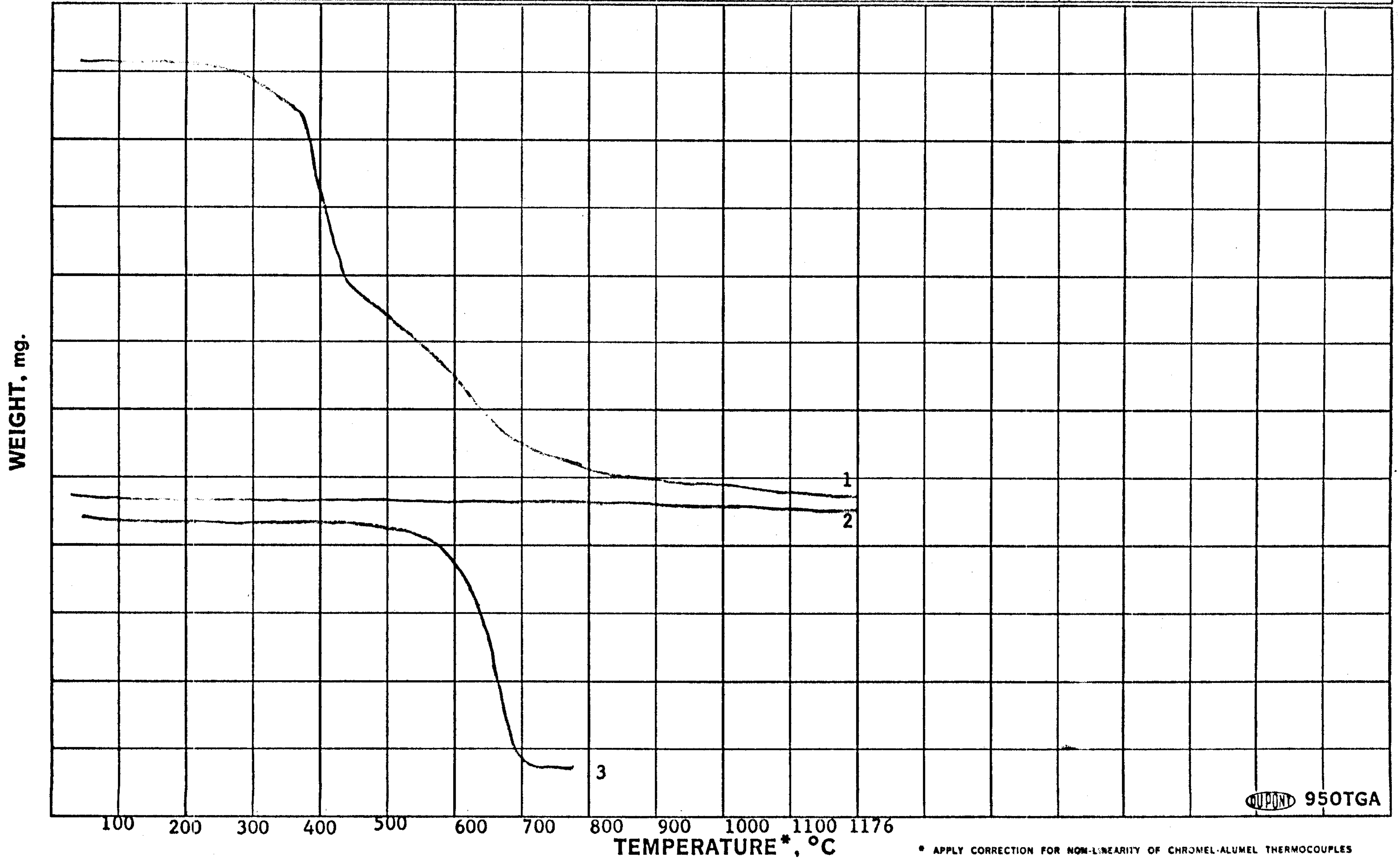


SAMPLE: RUN NO.:

*SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

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

SAMPLE: DA-39-34	X-AXIS	Y-AXIS	RUN NO. ____ DATE 12-7-65.
	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch	OPERATOR RKS
yellow polymer	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C/min.
			ATM. 1) N_2; 2) N_2; 3) air
SIZE 10.15 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.

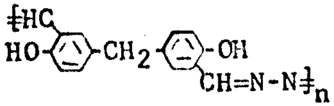


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 24

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

SAMPLE: DA-39-93



yellow polymer

SIZE 9.75 mg.

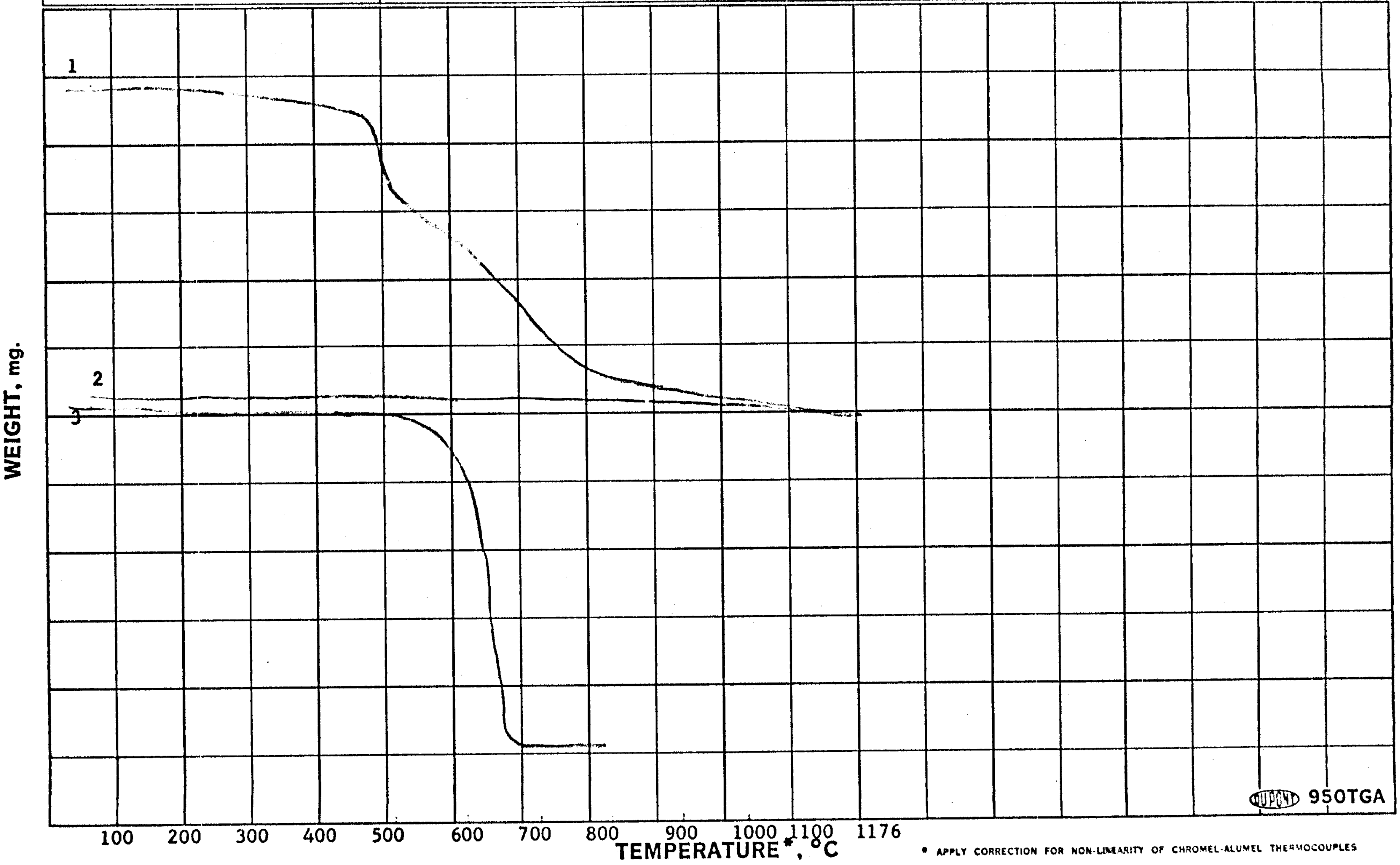
X-AXIS

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.

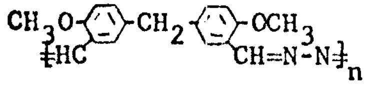
RUN NO.
DATE 12-8-65
OPERATOR RKS
HEATING RATE 15 °C/min.
ATM. 1) N_2; 2) N_2; 3) air
TIME CONSTANT 2 sec.



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

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

SAMPLE: DA-39-95


$CH_3O-C_6H_3(-CH=)-CH_2-C_6H_3(-OCH_3)-CH=N-N=$, n

yellow polymer

SIZE 10 mg.

X-AXIS

TEMP. SCALE 200 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 0 mg.

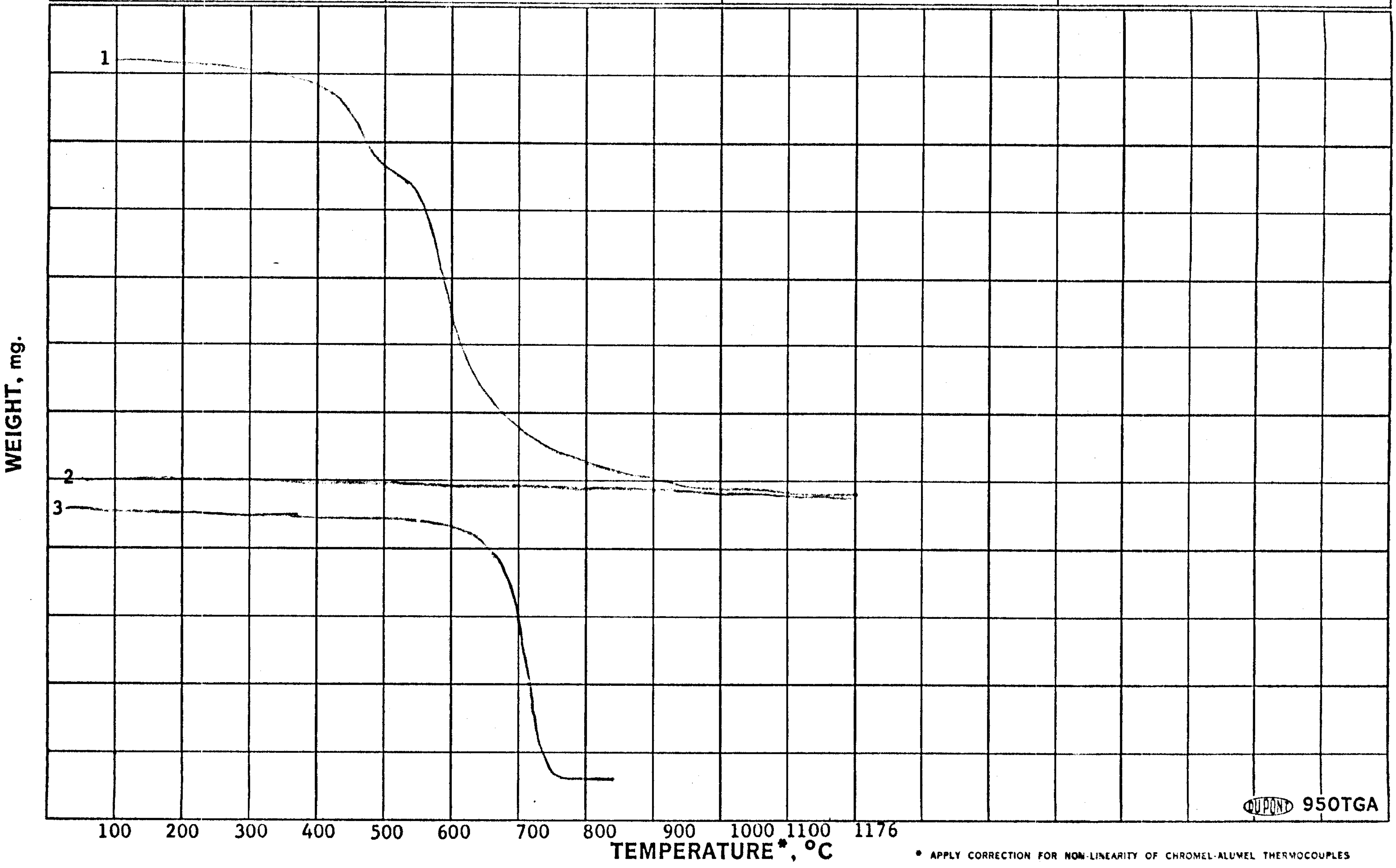
RUN NO. ______ DATE 12-8-65

OPERATOR RKS

HEATING RATE 15 °C/min.

ATM. 1) N$_2$; 2) N$_2$; 3) air

TIME CONSTANT 0 sec.

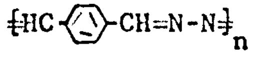


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 25

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

SAMPLE: DA-39-34


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

yellow polymer

SIZE 10;17 mg.

X-AXIS

TEMP. SCALE 100 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

SCALE 1 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 4.17 mg.

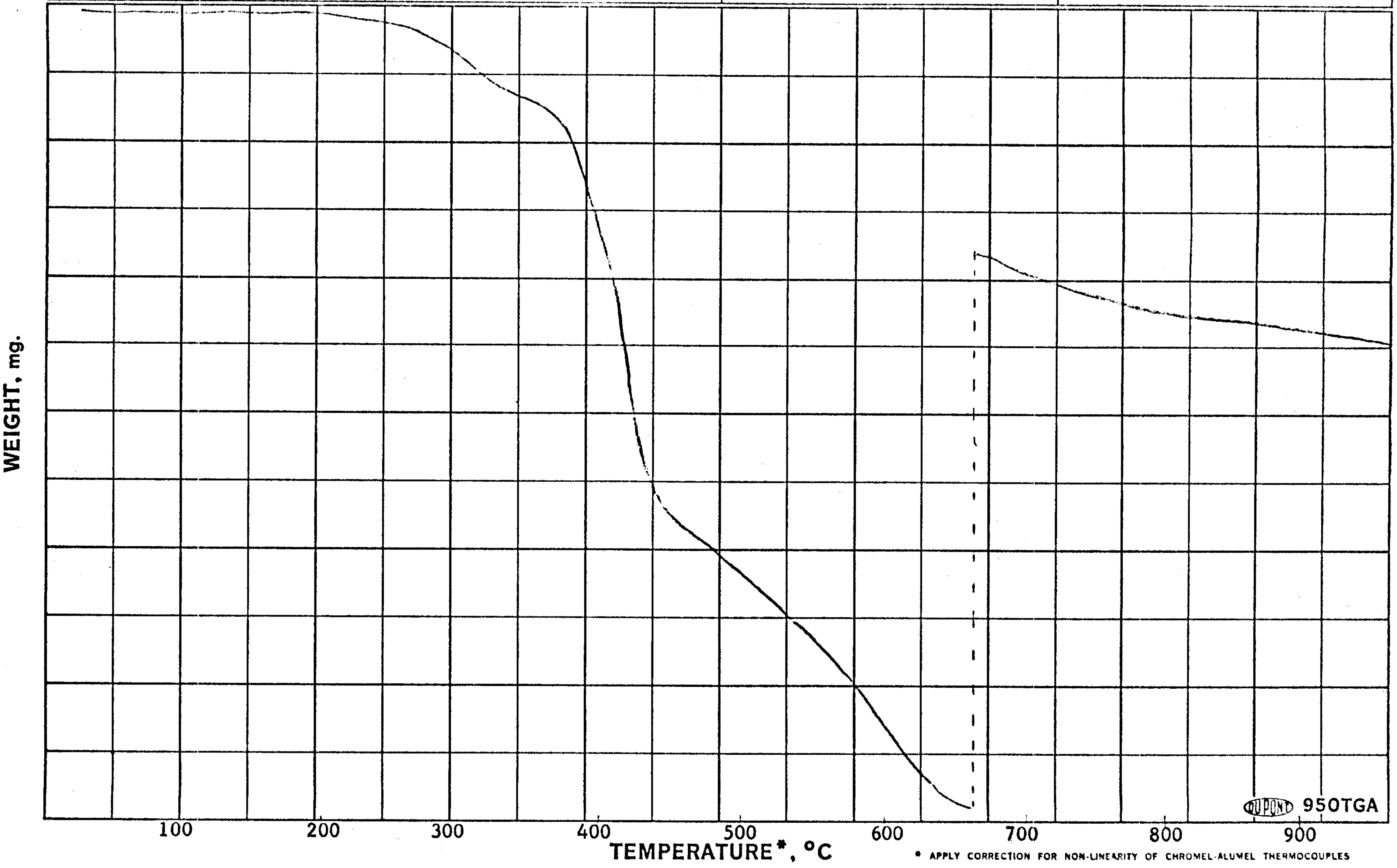
RUN NO. DATE 12-20-65

OPERATOR RKS

HEATING RATE 5 °C/min.

ATM. nitrogen

TIME CONSTANT 2 sec.

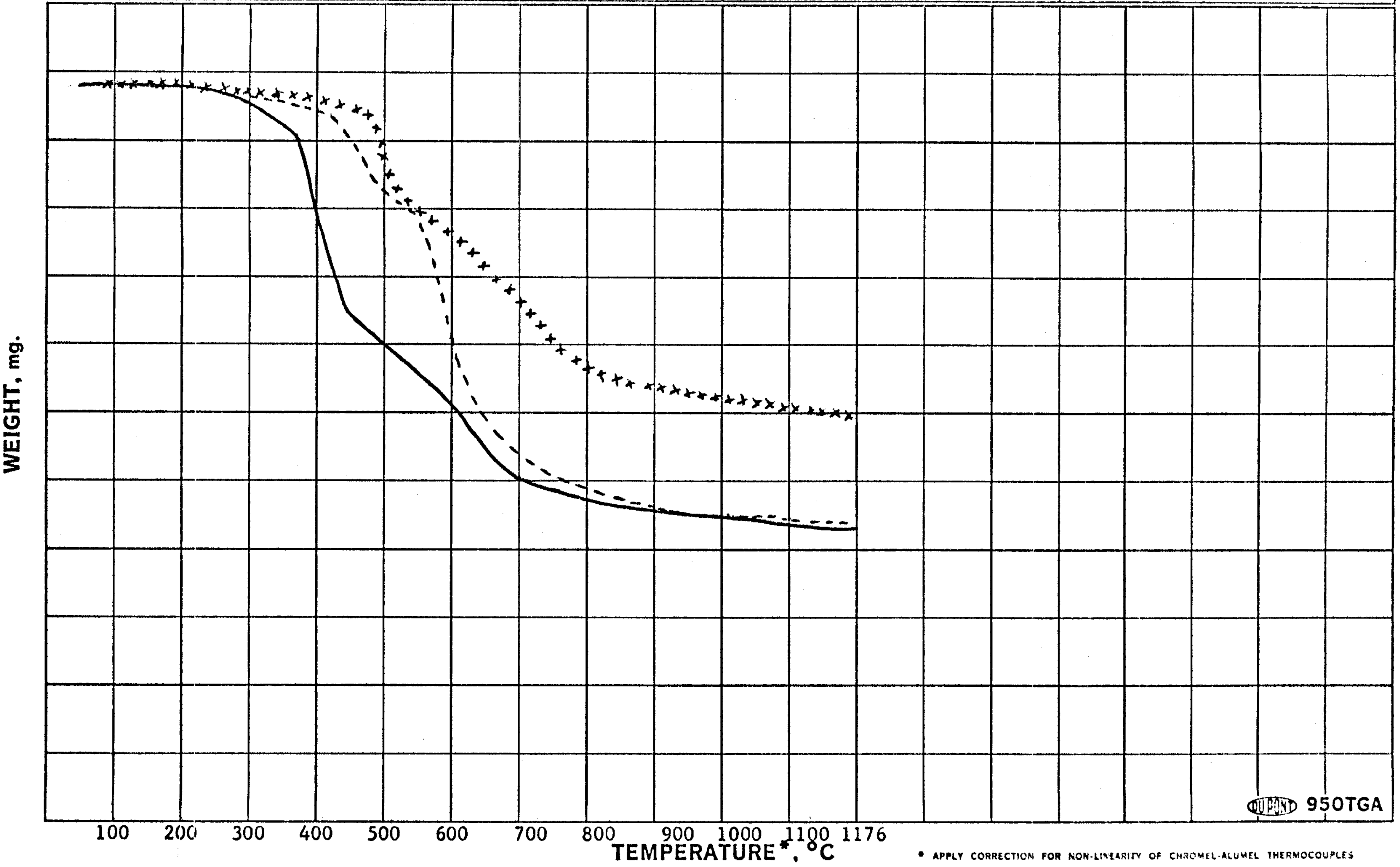


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 26

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

SAMPLE:	**X-AXIS**	**Y-AXIS**	**RUN NO.** ____ **DATE** 1-30-66
DA-39-34 ————————	**TEMP. SCALE** 200 °C/inch	**SCALE** 2 mg./inch	**OPERATOR** RKS
DA-39-93 xxxxxxxxxxxx	**SHIFT** 0 inch	(SCALE SETTING X 2)	**HEATING RATE** 15 °C/min.
DA-39-95 ------------			**ATM.** nitrogen
SIZE ____ mg.	**TIME SCALE (ALT.)** 0	**SUPPRESSION** 0 mg.	**TIME CONSTANT** 2 sec.



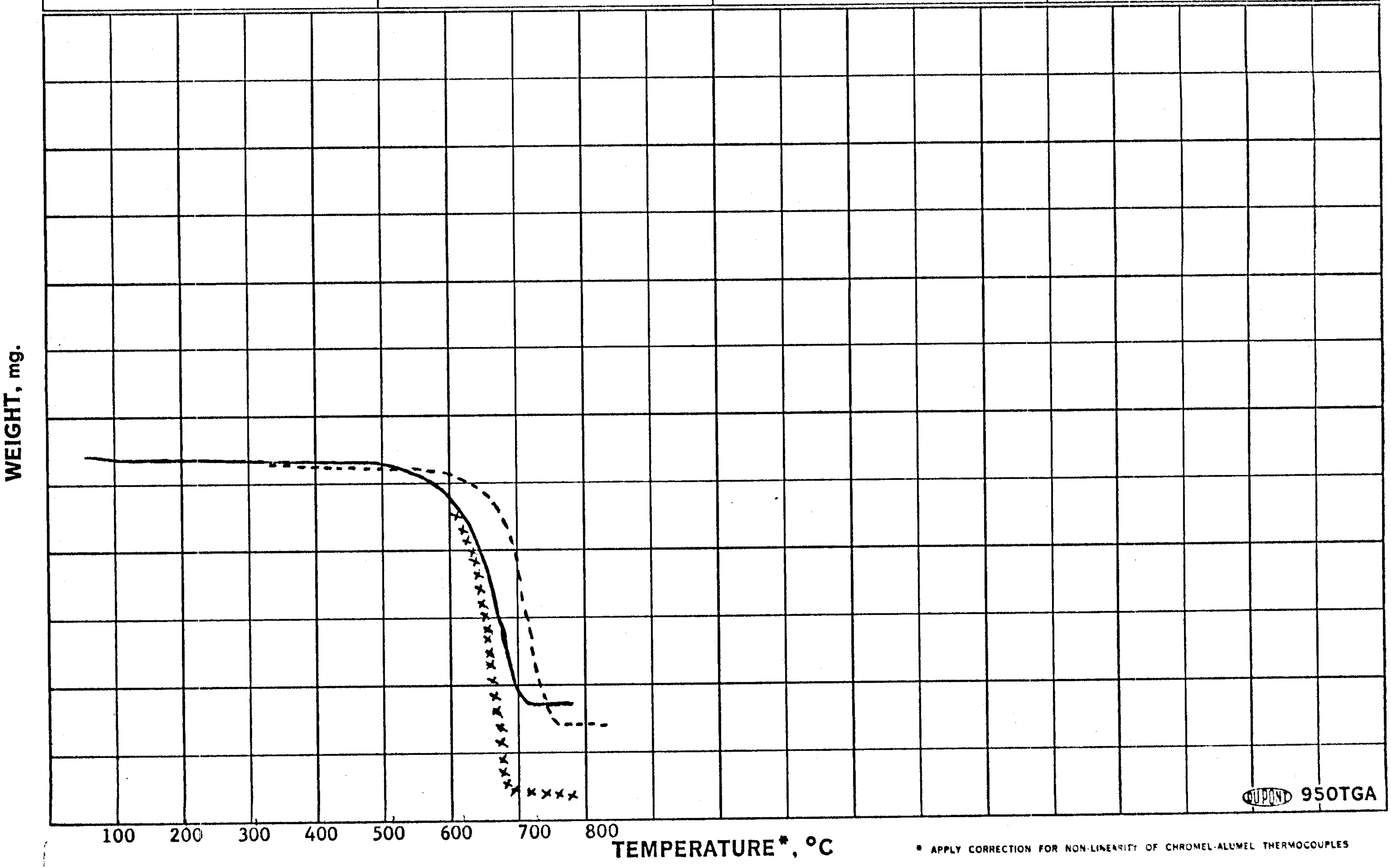
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 27

Appendix No. 28

INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

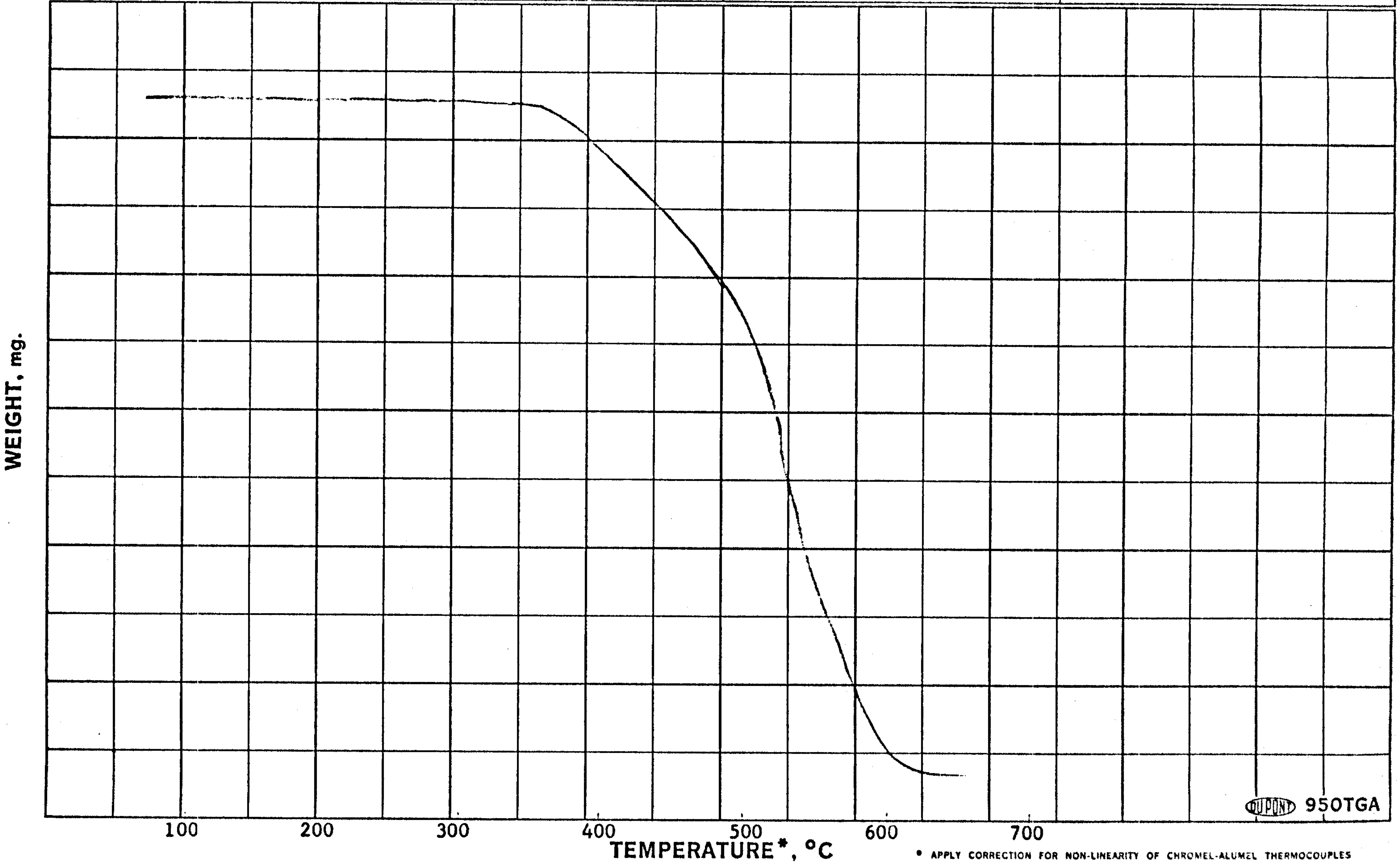
SAMPLE: DA-39-34 ———————— DA-39-93 xxxxxxxxxxxx DA-39-95 - - - - - - - - - - - - **SIZE** ____ mg.	**X-AXIS** **TEMP. SCALE** 200 °C/inch **SHIFT** 0 inch **TIME SCALE (ALT.)** 0	**Y-AXIS** **SCALE** 2 mg./inch (SCALE SETTING X 2) **SUPPRESSION** 0 mg.	**RUN NO.** ____ **DATE** 1-30-66 **OPERATOR** RKS **HEATING RATE** 15 °C/min. **ATM.** air (after 2 N_2 cycles) **TIME CONSTANT** 2 sec.



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

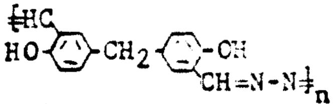
E. I. DU PONT DE NEMOURS & CO. (INC.)
INSTRUMENT PRODUCTS DIVISION
WILMINGTON 98, DELAWARE

SAMPLE:	X-AXIS	Y-AXIS	
SAMPLE: DA-39-34 $\{\text{HC-⌬-CH=N-N}\}_n$ yellow polymer	**TEMP. SCALE** 100 °C/inch	**SCALE** 2 mg./inch **(SCALE SETTING X 2)**	**RUN NO.** ____ **DATE** 1-11-66 **OPERATOR** RKS
	SHIFT 0 inch		**HEATING RATE** 15 °C/min. **ATM.** air
SIZE 9.95 mg.	**TIME SCALE (ALT.)** 0	**SUPPRESSION** 0 mg.	**TIME CONSTANT** 2 sec.



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

SAMPLE: DA-39-93



$$\left[HC\!\!-\!\!C_6H_3(OH)\!-\!CH_2\!-\!C_6H_3(-CH)(-CH{=}N\!-\!N)\right]_n$$

yellow polymer

SIZE 1) 10.08 2) 10.45 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 1-18-66

OPERATOR RKS

HEATING RATE 15 °C/min.

ATM. air

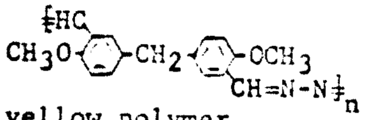
TIME CONSTANT 2 sec.

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

Appendix No. 31

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

SAMPLE: DA-39-95


$\left[HC(C_6H_3(OCH_3))-CH_2-C_6H_3(OCH_3)-CH{=}N-N\right]_n$

yellow polymer

SIZE 10.0 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.

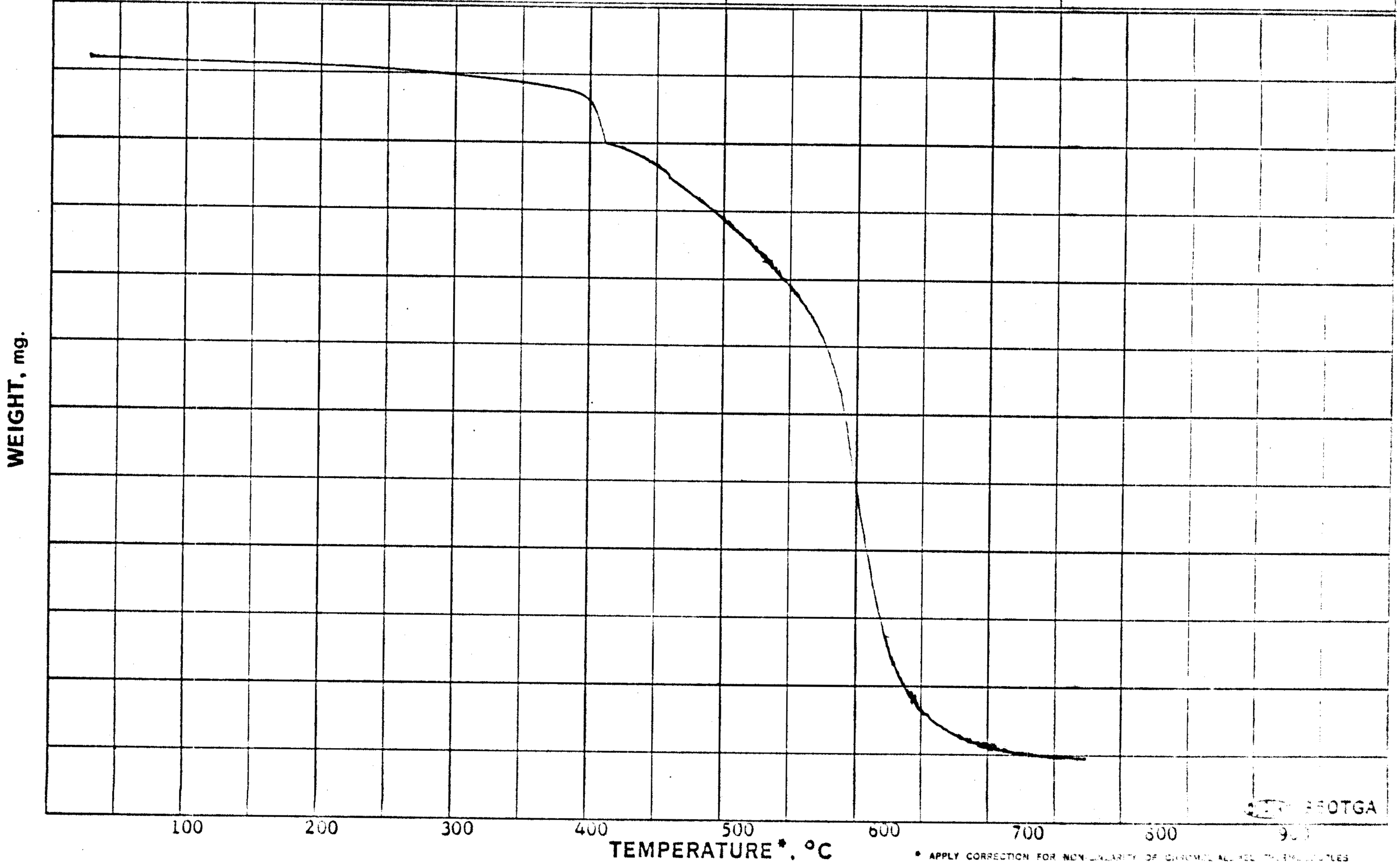
DATE 12-9-65

OPERATOR RKS

HEATING RATE 15 °C/min.

ATM. air

TIME CONSTANT 2 sec.

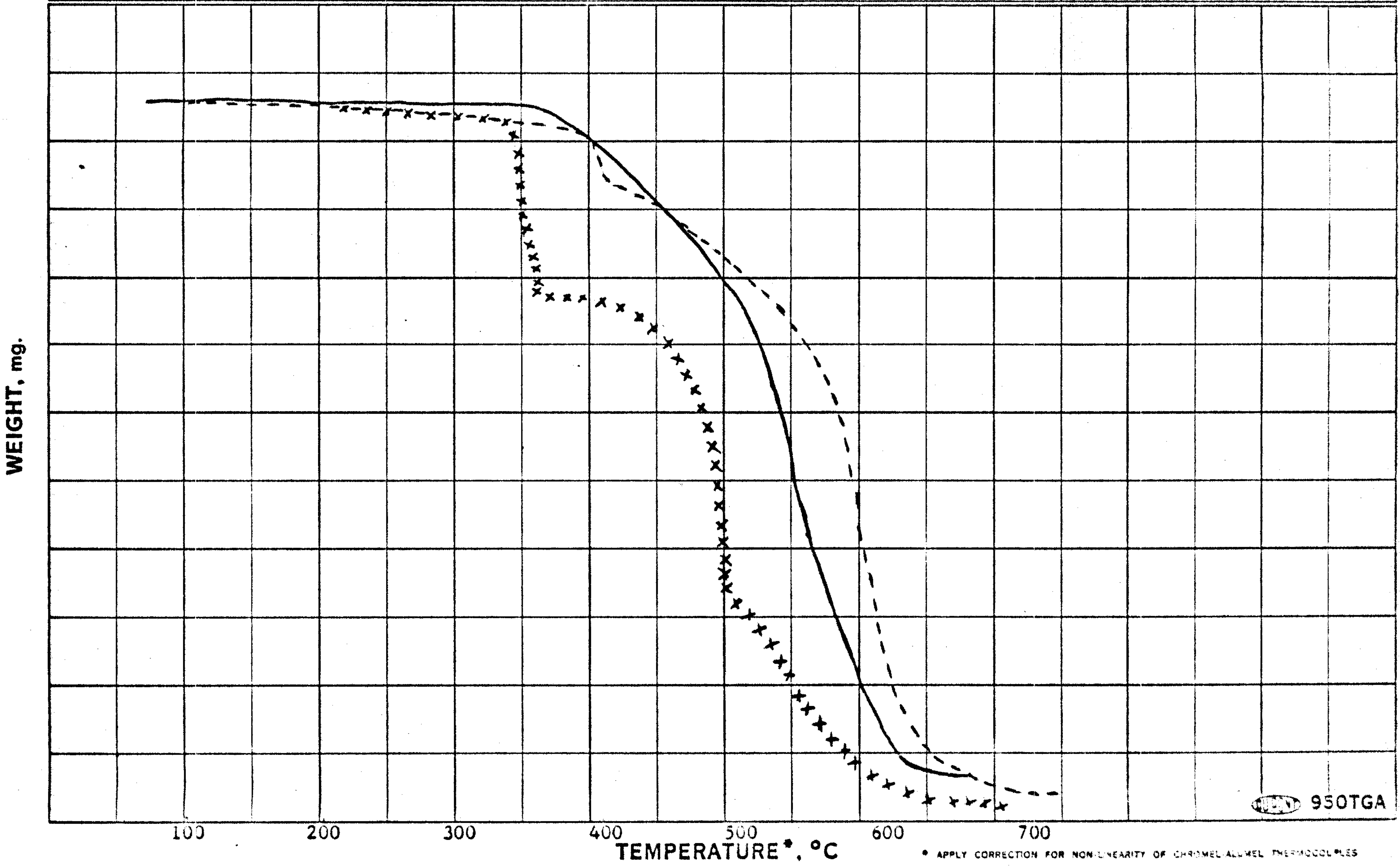


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

Appendix No. 32

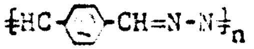
DU PONT | INSTRUMENT PRODUCTS DIVISION

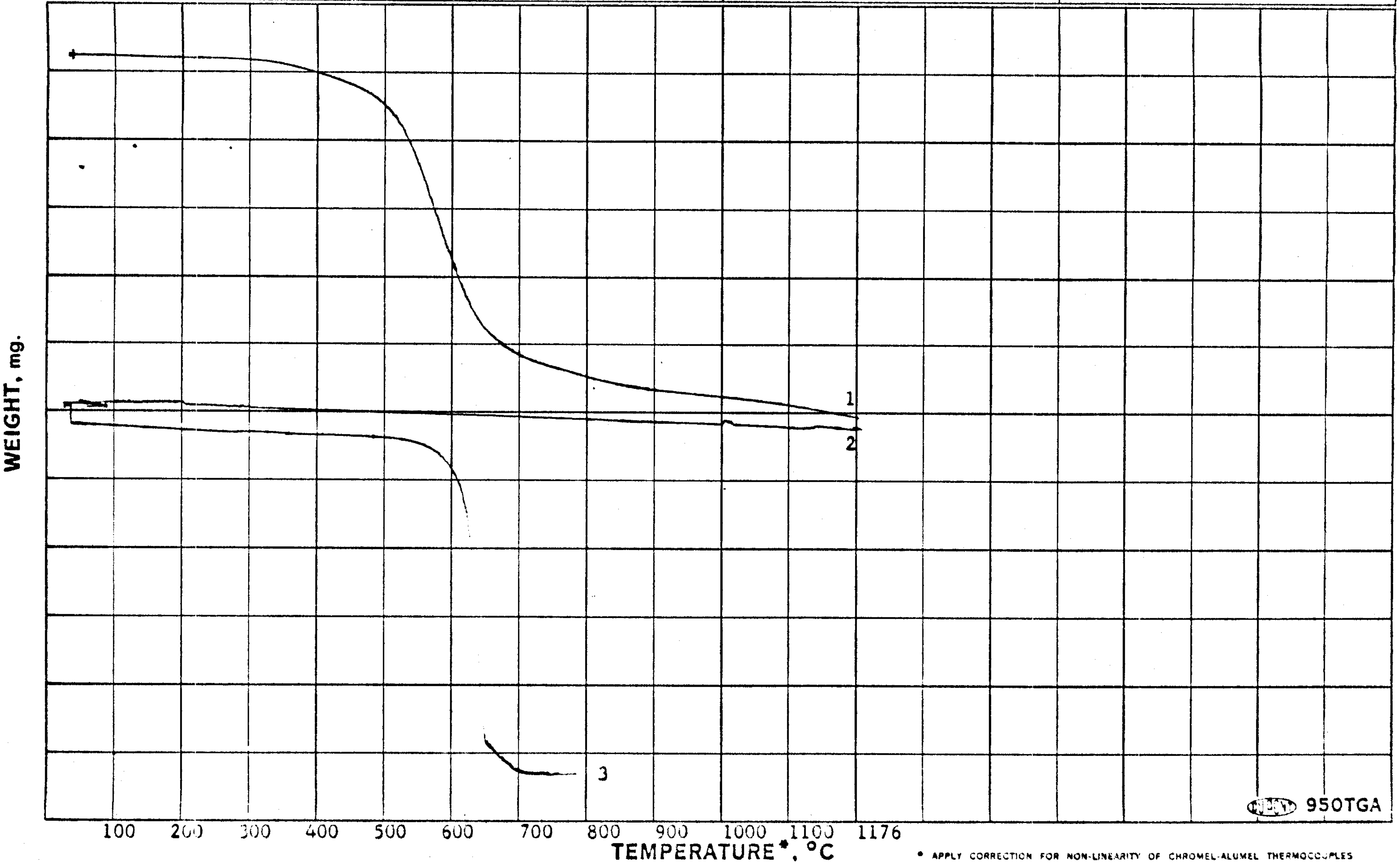
SAMPLE:	X-AXIS	Y-AXIS	
——— DA-39-34	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch	RUN NO. ____ DATE 1-18-66
xxxxxxxxx DA-39-93	SHIFT 0 inch	(SCALE SETTING X 2)	OPERATOR RKS
--------- DA-39-95			HEATING RATE 15 °C/min.
			ATM. air
SIZE ____ mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



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

INSTRUMENT PRODUCTS DIVISION
WILMINGTON, DELAWARE

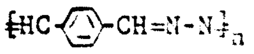
SAMPLE: DA-39-45(a)-p	X-AXIS	Y-AXIS	RUN NO. ______ DATE 12-11-65
	TEMP. SCALE 200 °C/inch	SCALE 2 mg./inch	OPERATOR RKS
black	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C/min.
			ATM. 1) N_2; 2) N_2; 3) air
SIZE 9.90 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



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

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

SAMPLE: DA-39-45(a)-m



black

SIZE 9.80 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.

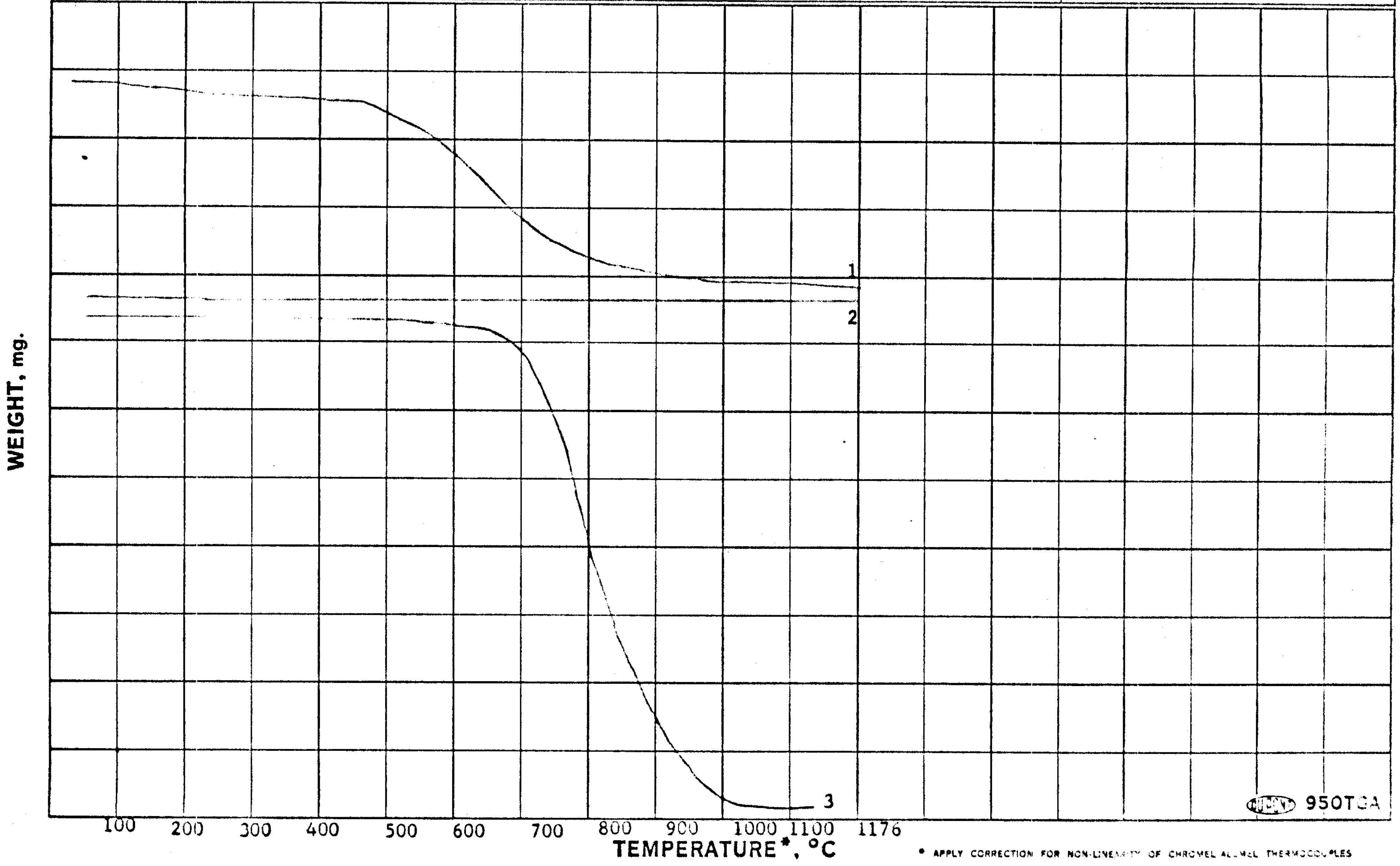
RUN NO. ______ **DATE** 12-13-65

OPERATOR RKS

HEATING RATE 15 °C/min.

ATM. 1) N_2; 2) N_2; 3) air

TIME CONSTANT 2 sec.

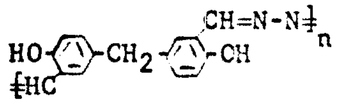


* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

Appendix No. 34

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

SAMPLE: DA-39-97



black

SIZE 10.0 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.

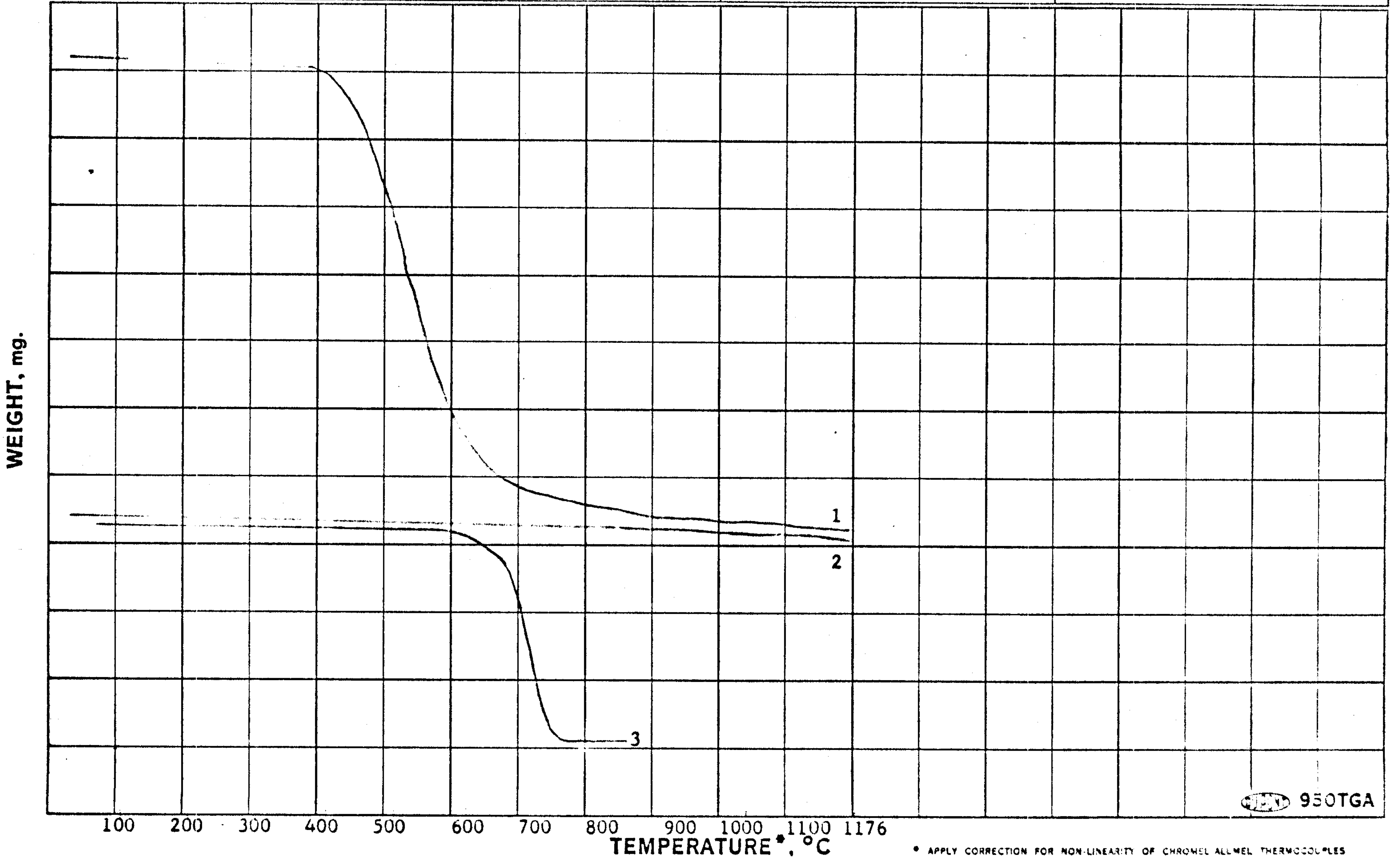
RUN NO. DATE 12-16-65

OPERATOR RKS

HEATING RATE 15 °C/min.

ATM. 1) N_2; 2) N_2; 3) air

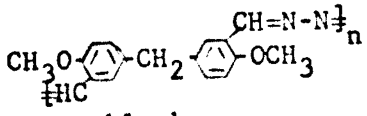
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

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

SAMPLE: DA-39-99



black

SIZE 10.0 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 12-3-65

OPERATOR RKS

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

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

SAMPLE:
———— DA-39-45(a) powder
••••••••• DA-39-45(a) mass
xxxxxxxxx DA-39-97 hydroxy
--------- DA-39-99 methoxy

SIZE ______ mg.

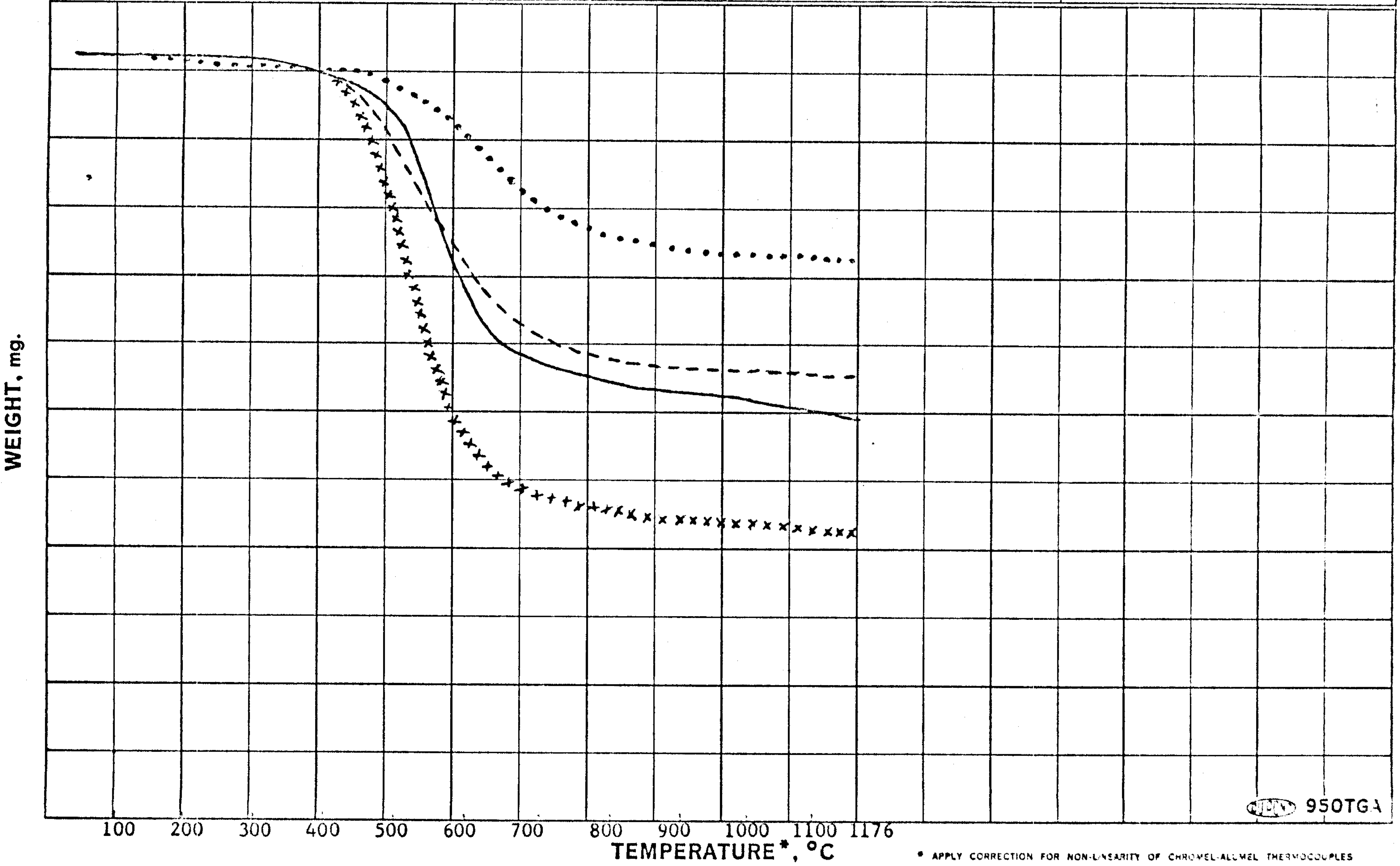
X-AXIS

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.

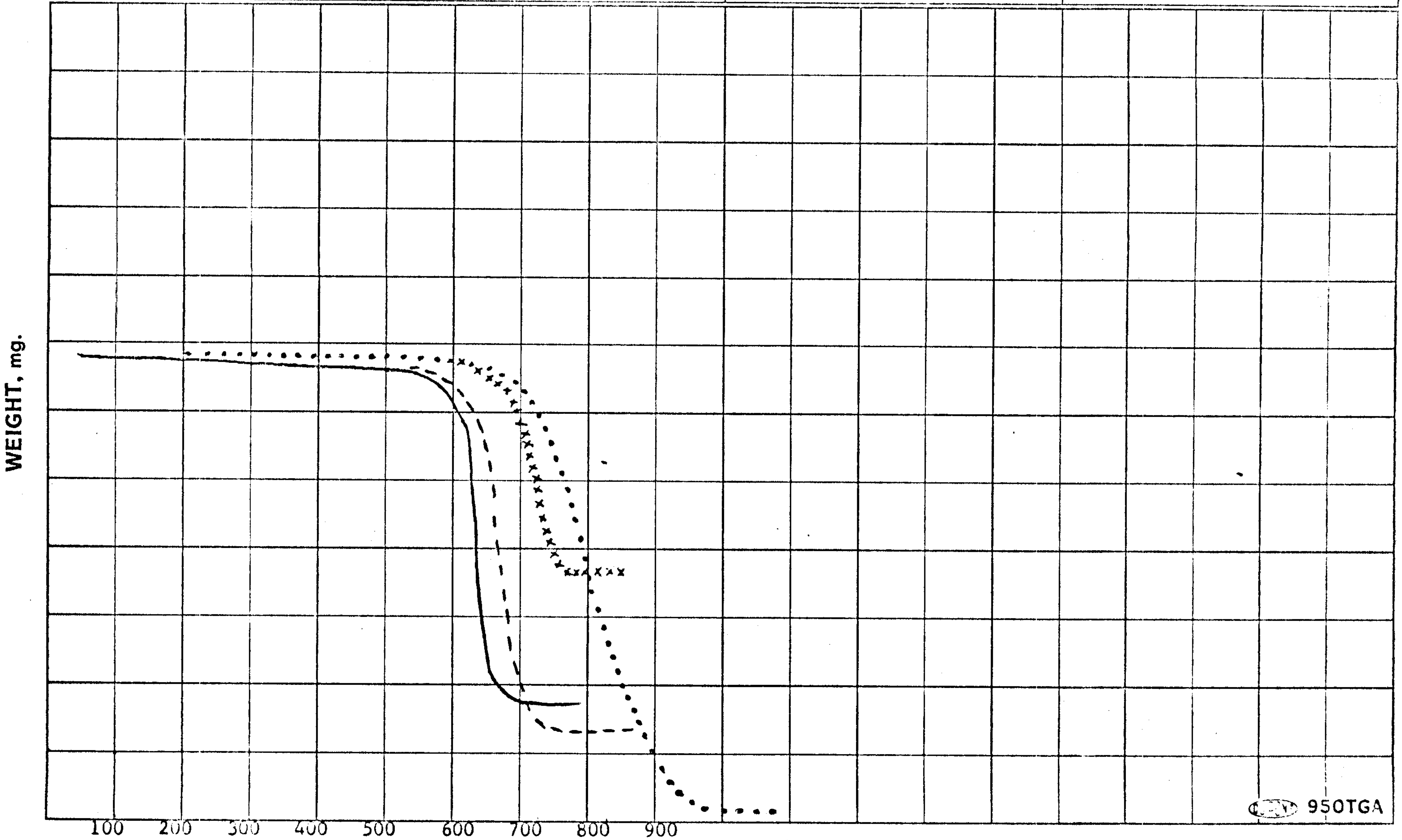
RUN NO. ______ DATE 1-30-66
OPERATOR RKS
HEATING RATE 15 °C/min.
ATM. nitrogen
TIME CONSTANT 2 sec.



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

INSTRUMENT PRODUCTS DIVISION

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. ____ DATE 1-30-66
——— DA-39-45(a)-p ········· DA-39-45(a)-m xxxxxxxxx DA-39-97 --------- DA-39-99	TEMP. SCALE 200 °C/inch SHIFT 0 inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR RKS HEATING RATE 15 °C/min. ATM. air; after 2 N_2 cycles
SIZE ____ mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.

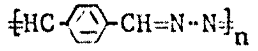


TEMPERATURE*, °C

* 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-39-45(a)-p



black

SIZE 9.80 mg.

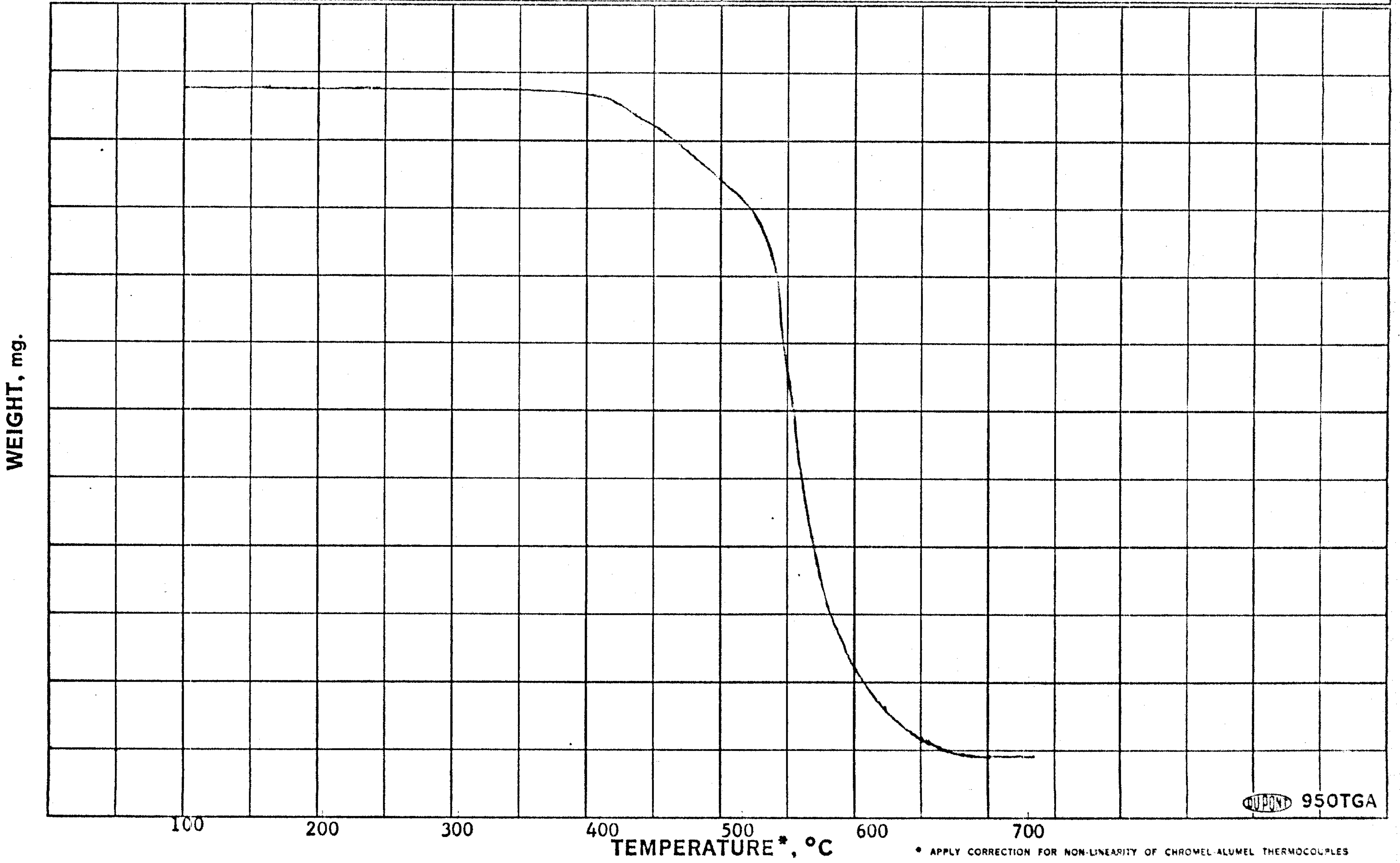
X-AXIS

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

Y-AXIS

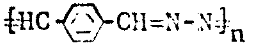
SCALE 2 mg./inch
(SCALE SETTING X 2)
SUPPRESSION 0 mg.

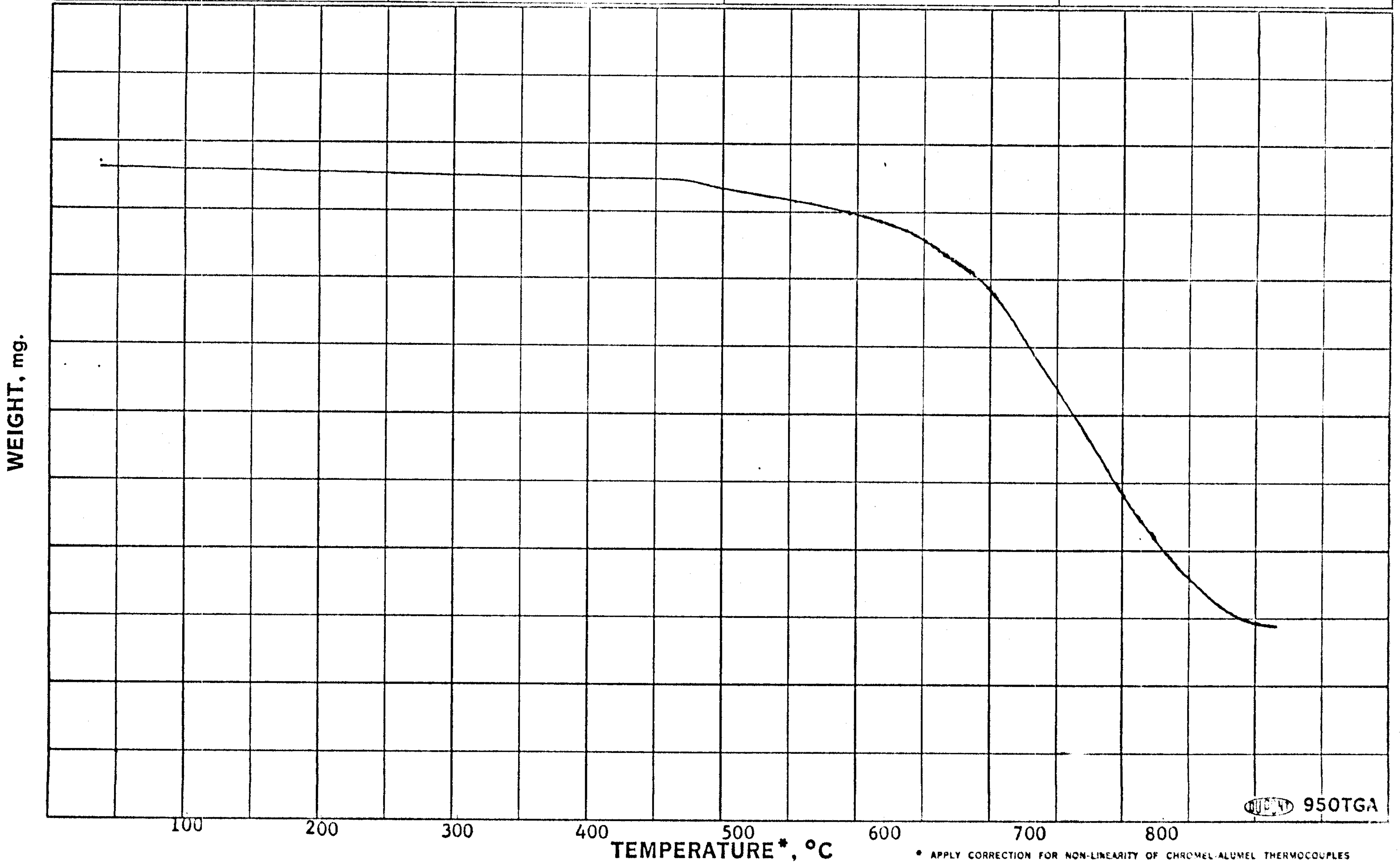
RUN NO. **DATE** 12-10-65
OPERATOR RKS
HEATING RATE 15 °C/min.
ATM. air
TIME CONSTANT 2 sec.



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

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

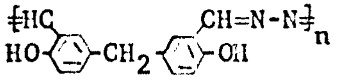
SAMPLE: DA-39-45(a)-m	X-AXIS	Y-AXIS	RUN NO. ____ DATE 12-9-65
	TEMP. SCALE 100 °C/inch	SCALE 4 mg./inch	OPERATOR RKS
black	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C/min.
SIZE 14.40 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	ATM. air
			TIME CONSTANT 2 sec.



* 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-39-97



black

SIZE 10.0 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.

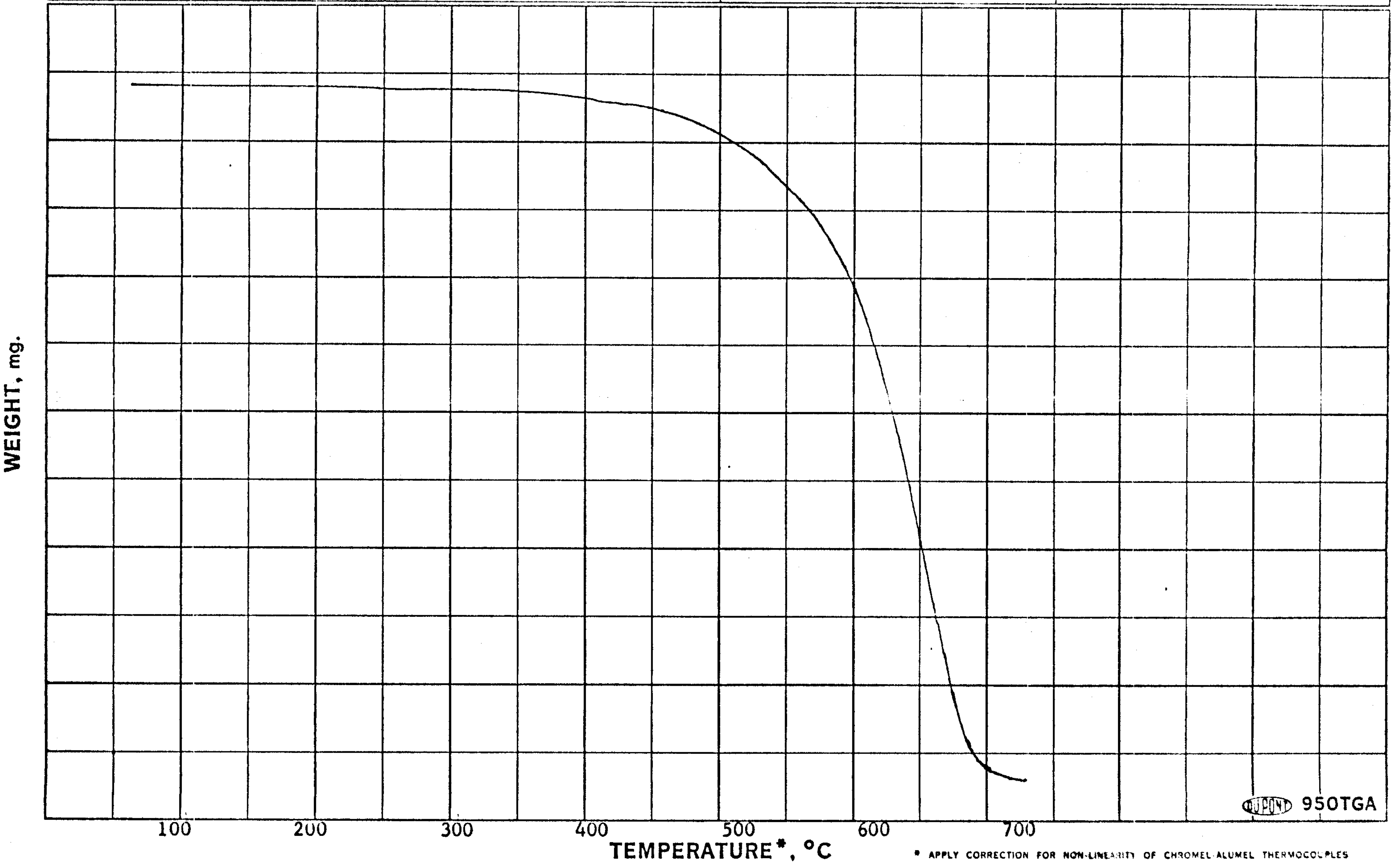
DATE 12-9-65

OPERATOR RKS

HEATING RATE 15 °C/min.

ATM. air

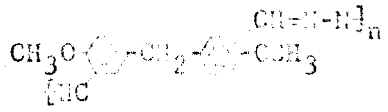
TIME CONSTANT 2 sec.



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

INSTRUMENT PRODUCTS DIVISION

SAMPLE: DA-39-99



CH_3O-C$_6$H$_4$-CH_2-C$_6$H$_4$-OCH_3 [HC=N-N]$_n$

black

SIZE 11.48 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.

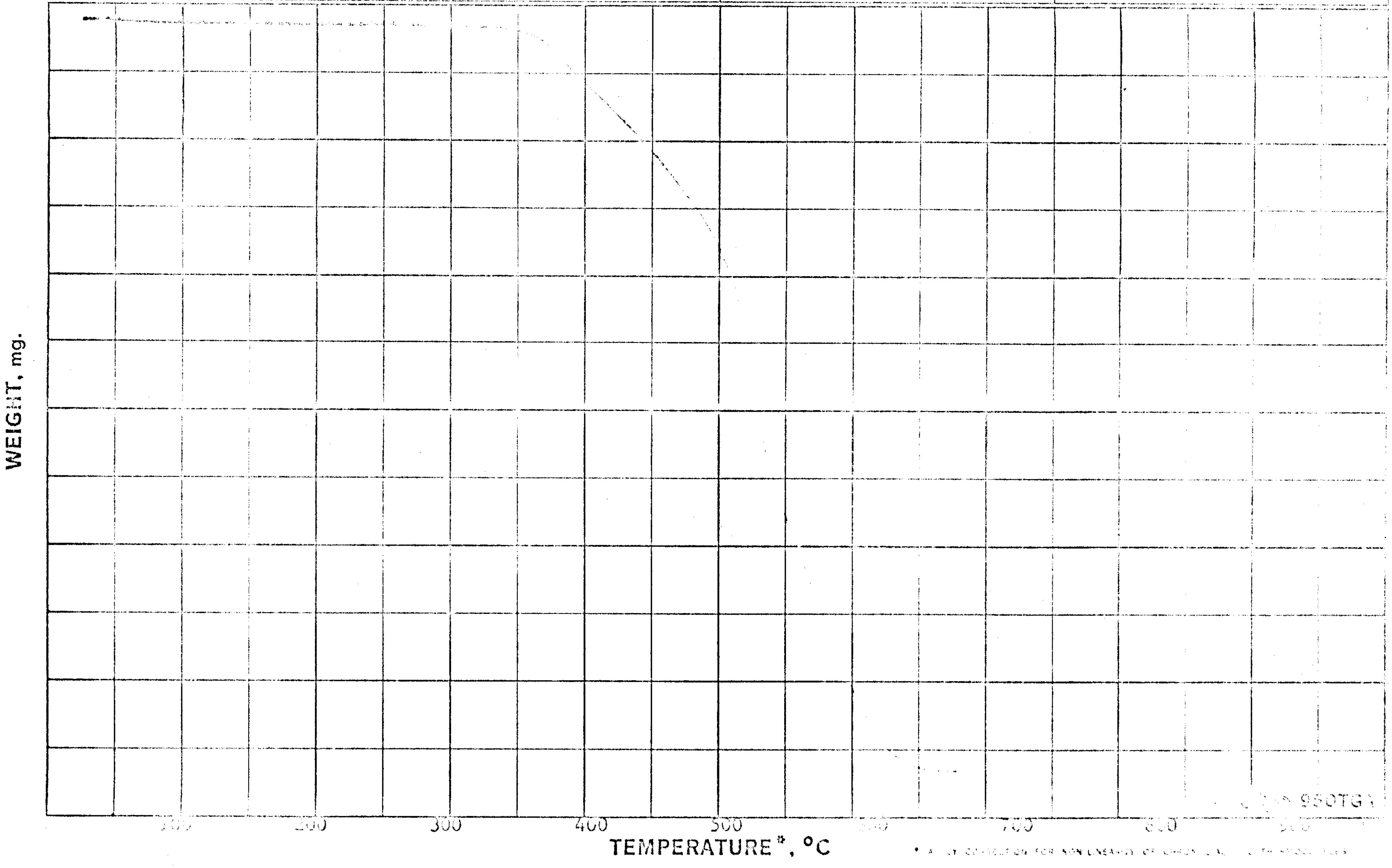
RUN NO. DATE [illegible]

OPERATOR [illegible]

HEATING RATE 15 °C/min.

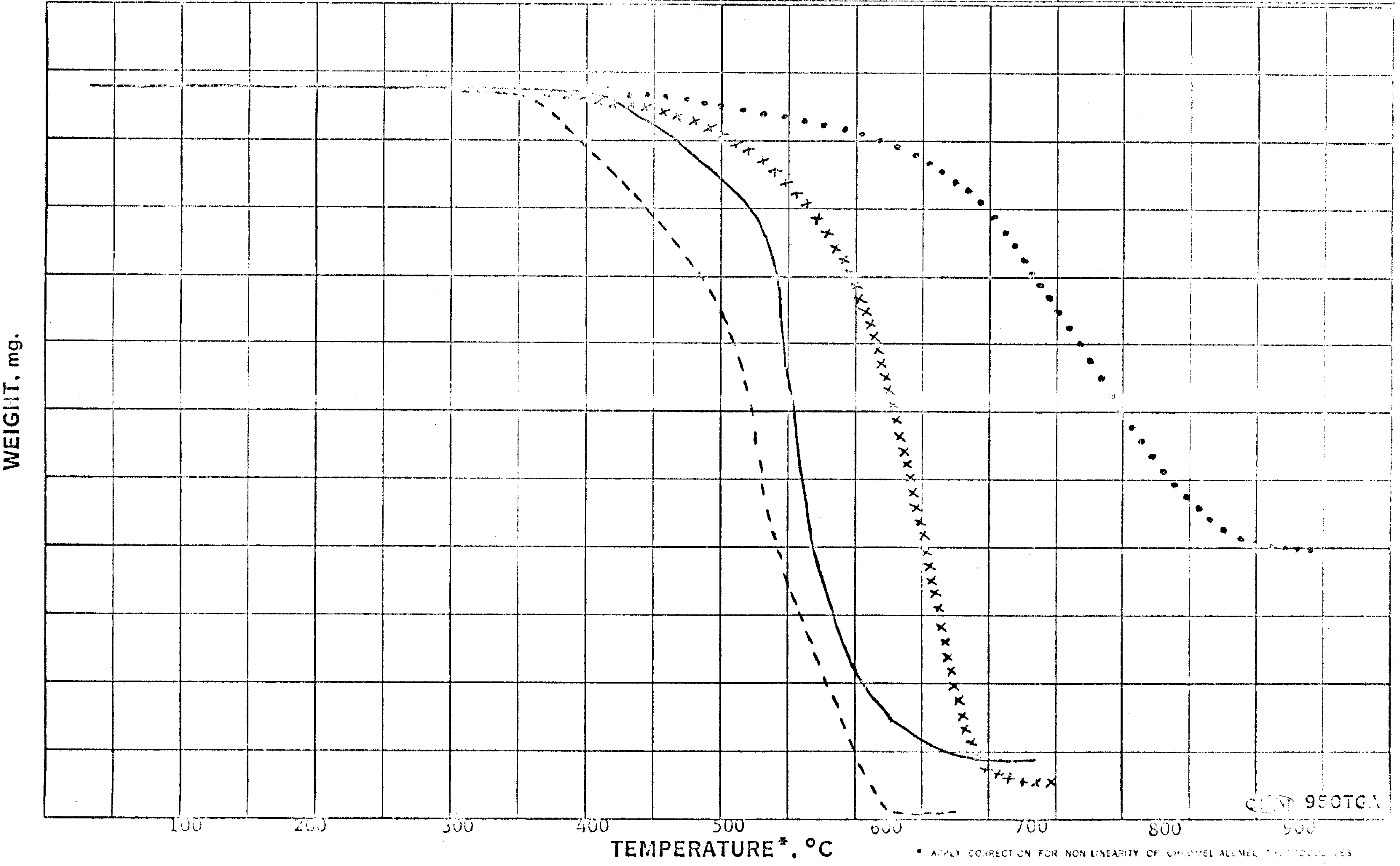
ATM. air

TIME CONSTANT 2 sec.



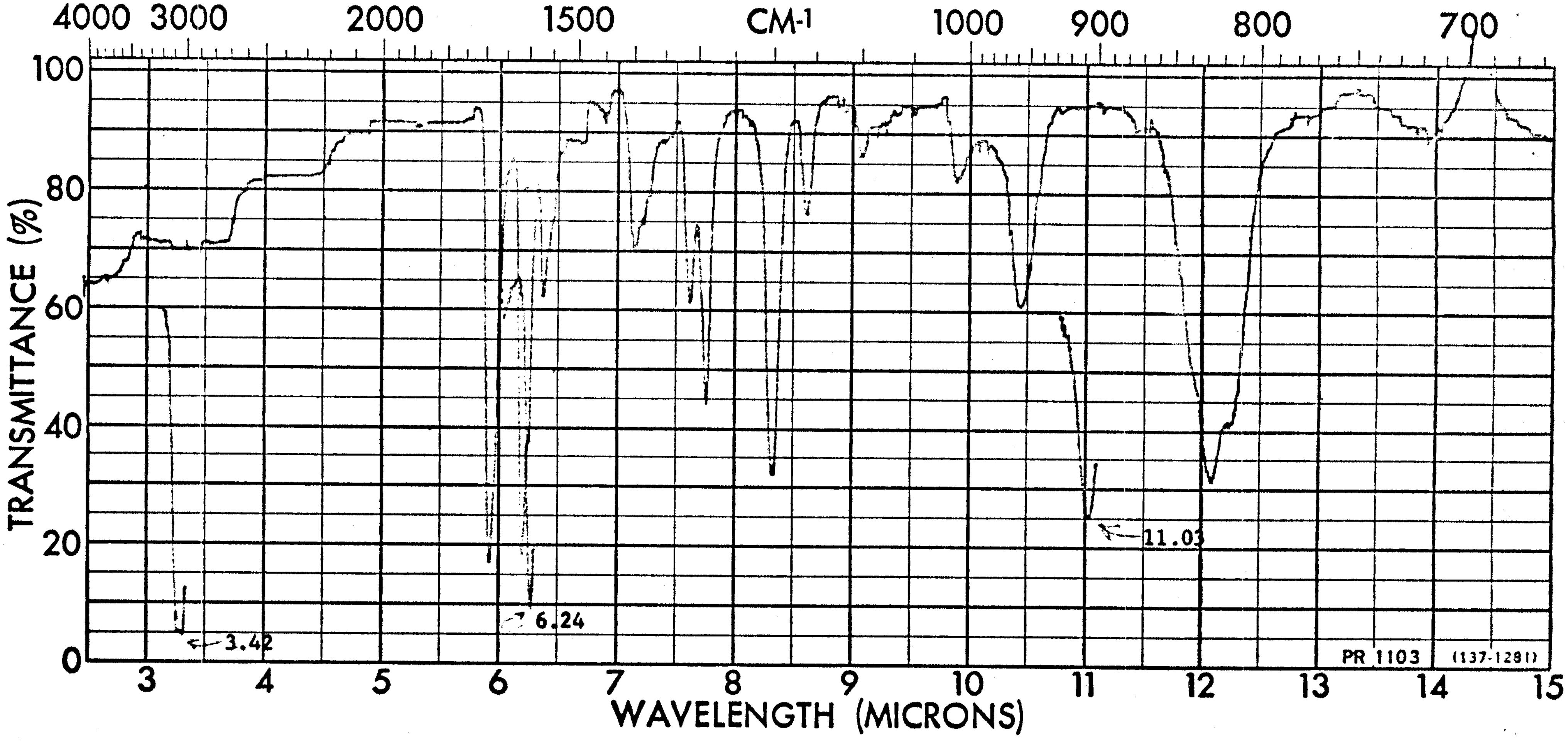
INSTRUMENT PRODUCTS DIVISION

SAMPLE:	X-AXIS	Y-AXIS	RUN NO. ____ DATE 1-30-66
———— DA-39-45(a) powder ········ DA-39-45(a) mass xxxxxxxx DA-39-97 hydroxy -------- DA-39-99 methoxy	TEMP. SCALE 100 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR [illegible]
	SHIFT 0 inch		HEATING RATE 15 °C/min.
			ATM. air
SIZE ____ mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	TIME CONSTANT 2 sec.



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

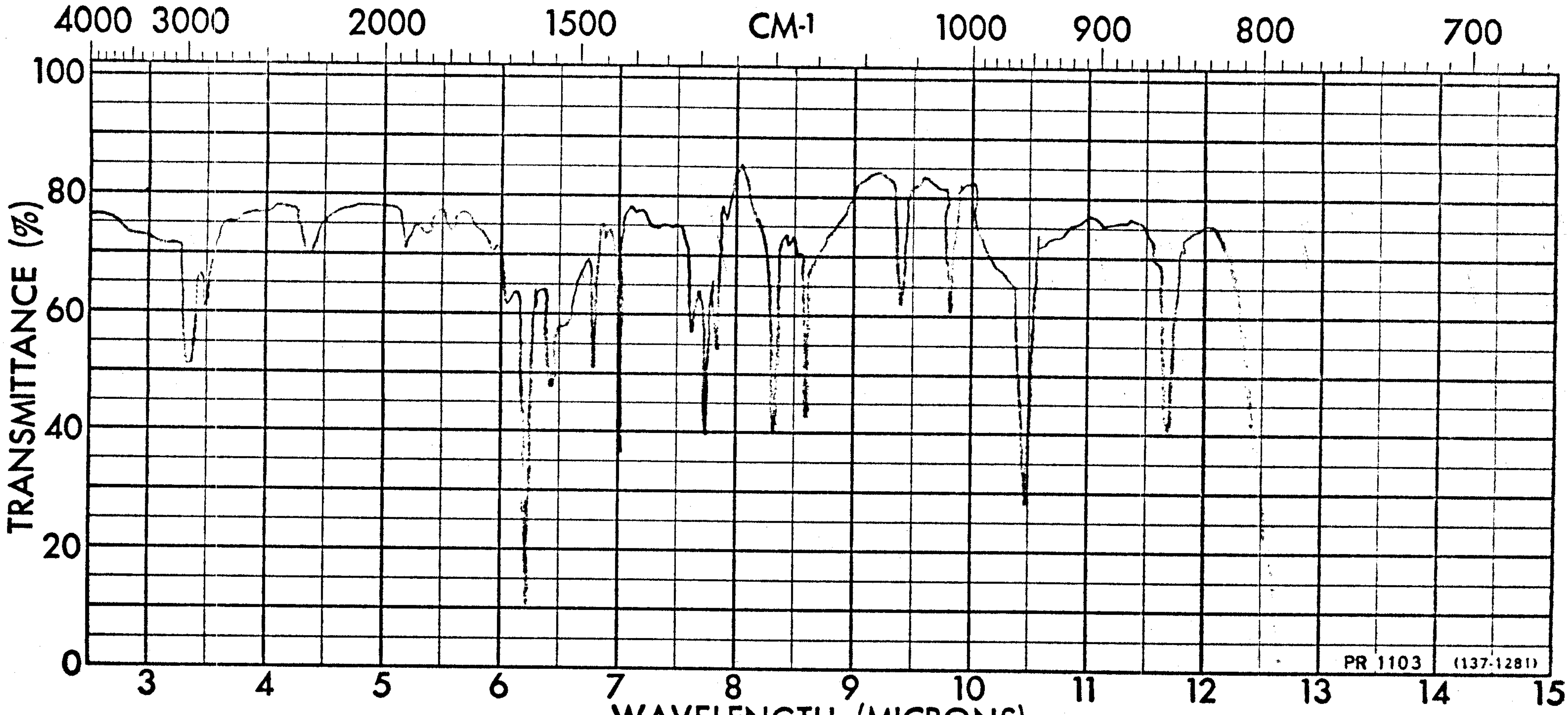
Appendix No. 44

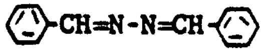


IR of DA-39-34 

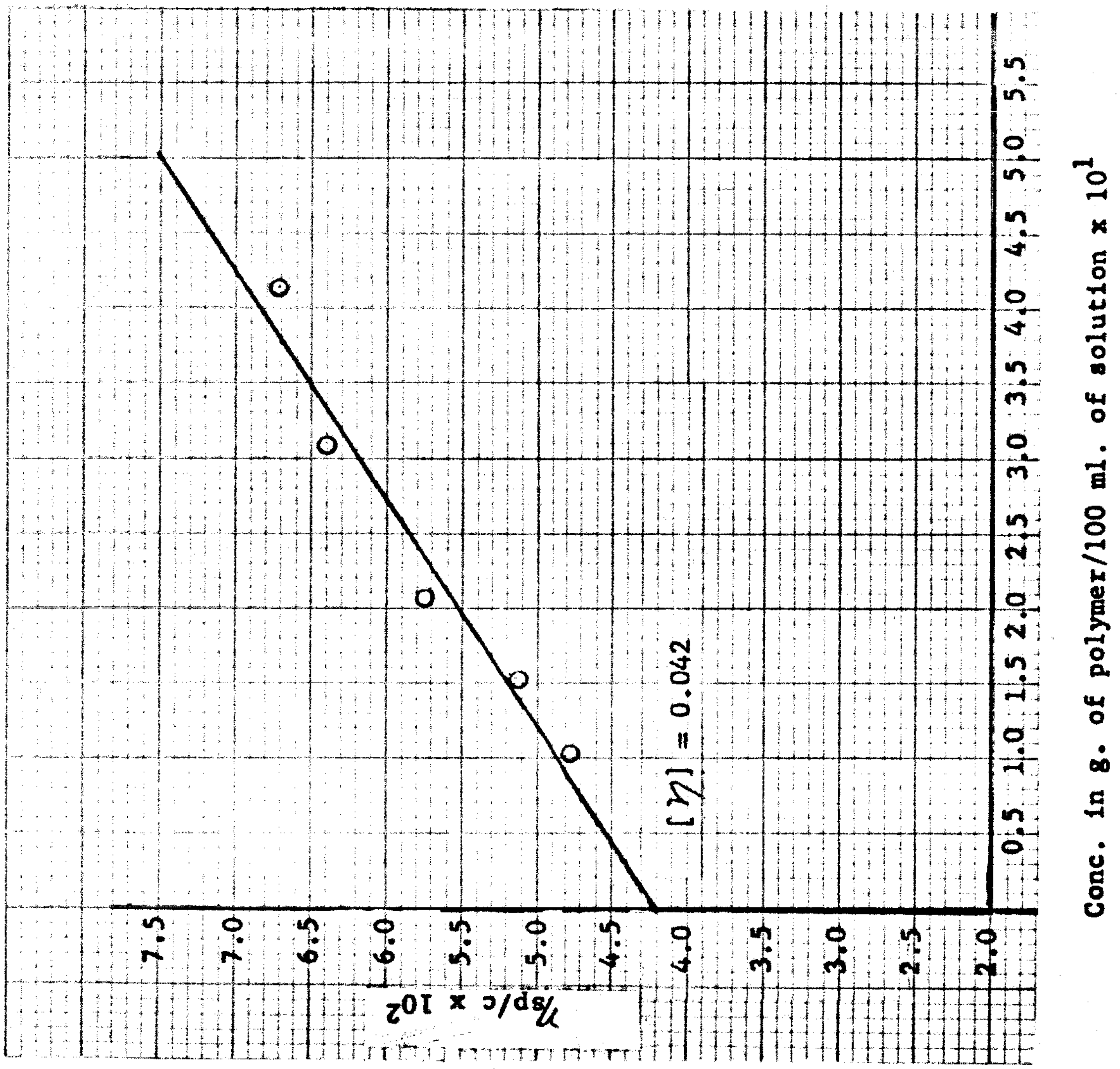
KBr Pellet 2-8-66

Appendix No. 45





CCl_4 Solution 2-26-65


$\eta_{sp}/c \times 10^2$
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
$[\eta] = 0.042$
Conc. in g. of polymer/100 ml. of solution x 10^1