REPORT

NUMBER ELEVEN

ON

THE

FUNDAMENTAL STUDIES ON THE SYNTHESIS OF HEAT-RESISTANT POLYMERS

TO

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

WASHINGTON, D.C.

PERFORMED

UNDER

NASA GRANT NsG339

SEPTEMBER, 1966

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA 46556

PROGRESS REPORT NUMBER 11

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FUNDAMENTAL STUDIES ON THE SYNTHESIS OF HEAT-RESISTANT POLYMERS

EXPLORATORY STUDIES ON THE SYNTHESIS OF POLYMERIC AZINES

PERFORMED

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NASA GRANT NsG339

BY

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SEPTEMBER 15, 1966

FOREWORD

This report is a summary report of the researches performed under NASA Grant NsG339 for the period 31 January 1966 to 15 September 1966 on the synthesis of heat-resistant polymers. The technical aspect of this grant is administered by Mr. Bernard Achhammer, Office of Advanced Research and Technology, NASA Headquarters, Washington, D. C. 20546.

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

This report covers studies performed by G. F. D'Alelio and Richard Schoenig. The technical assistance of P. R. Johnson and D. R. Rao for the period of June 15, 1966 to September 1, 1966 is acknowledged.

Date September 15, 1966

Signed G. F. D'Alelio

G. F. D'Alelio
Principal Investigator

ABSTRACT

Some kinetic parameters concerning the decomposition of the yellow, low molecular weight polyazines and the black, higher molecular weight azine polymers were investigated. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques were used, as required in the Freeman and Carroll method. This method yields the order of reaction and the energy of activation from examination of the weight loss TGA traces of the decomposing polymer. The supplemental method of Flynn and Wall, which yields approximate energies of activation from TGA plots, was also employed.

A direct one-step synthesis of a high molecular weight black polyazine which uses only simple constituent compounds was demonstrated and shown to be feasible.

Studies were initiated to attempt to determine molecular weights of black azine melt polymers by the method of end-group tagging with a characterizable moiety and subsequent elemental analysis for the presence of that group.

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EXPLORATORY STUDIES ON THE SYNTHESIS OF POLYMERIC AZINES

I. Introduction.

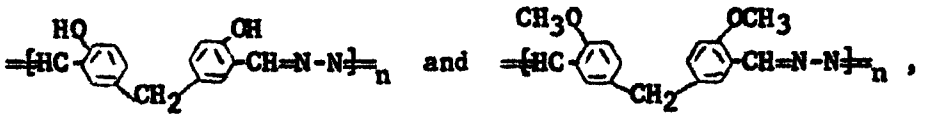
In two preceding reports[1,2] results concerning the syntheses and evaluations of monomeric and polymeric azines were presented. These results indicated that polymeric azines of the general formula, $-\{HC\text{-}Ar\text{-}CH=N\text{-}N\}-_n$, where Ar represents a divalent aromatic moiety, decompose at elevated temperatures (350-400°C) yielding a thermally stable polystilbene-type polymer, $-\{HC\text{-}Ar\text{-}CH\}-_n$. This reactivity in the polyazines was predicted on the basis of preliminary studies concerning the decomposition of azine monomers, which are known[3] to decompose as follows:

$$Ar\text{-}CH=N\text{-}N=HC\text{-}Ar \xrightarrow{\Delta} Ar\text{-}CH=HC\text{-}Ar + N_2\uparrow. \qquad \text{(eq. 1)}$$

The mechanism for the decomposition of the monomeric azine, set forth by Zimmerman and Somasekhara,[4] has been shown to be essentially an ionic chain mechanism involving phenyldiazomethane, $Ar\text{-}\overset{\ominus}{C}H\text{-}\overset{\oplus}{N}\equiv N$, as the chain-carrying species in a first order reaction. In order to determine whether this mechanism, operative in the monomeric decomposition, is also applicable in the case of the polymaric decomposition, the order of reaction and the energy of activation for the decomposition of the monomer, benzalazine, $C_6H_5CH=N-N=HCC_6H_5$, and the polymer, polybenzalazine, $-\{HCC_6H_4\text{-}CH=N\text{-}N\}-_n$, were obtained. The data on the polymer decomposition was obtained by application of the method of Freeman and Carroll[5] which utilizes plots of weight loss versus time obtained in a thermal gravimetric analysis of the polymer; and subsequent application of derived kinetic formulae yielded the order of reaction and the energy of activation.

In this report this method of kinetic evaluation is extended to two

different low molecular weight azine polymers,



in an attempt to determine the effects, if any, of such parameters as hydrogen bonding (O-H···N) on the order of reaction and energy of activation.

An analysis of the kinetic parameters of the black azine polymers prepared by a melt process was also attempted but this method failed to yield any conclusive results. A recent method for evaluation of the energy of activation for substances undergoing decomposition has been set forth by Flynn and Wall.[6] This relatively simple method gives approximate activation energies by a consideration of (1) a constant weight loss of the polymer, and (2) the corresponding temperatures at that constant weight loss as a function of the heating rate. This method was employed on the three yellow azine polymers previously mentioned in connection with the method of Freeman and Carroll.[5]

This report also contains preliminary studies to determine the approximate molecular weight of the black polyazine polymers by tagging these polymers with a characterizable end group such as fluorine and chlorine. It was contemplated that such a polymer might then be suitably purified and subsequently analyzed for the characteristic end group by elemental analysis. Such an analysis coupled with a knowledge of the repeating unit in the polymer should then enable an approximate molecular weight estimate to be made. It was also felt possible to arrive at some approximate condensation kinetics for the formation of the polyazine by determining the degree of polymerization, $\overline{DP}$, also from end group elemental analyses, as a function of time.

The feasibility of synthesizing directly a black polyazine polymer in

a reaction involving only the simplest compounds such as aniline, hydrazine, benzaldehyde and terephthaldehyde was also demonstrated.

II. Syntheses of Monomers.

In order to prepare azine polymers with suitable tagged end groups,

 and where X = F or Cl, and Y = F, a series of appropriately substituted monomers was synthesized.

A. Experimental.

1. (DA-39-106) Synthesis of 4,4'-Dichlorobenzalazine.

p-Chlorobenzaldehyde, 5.000 g. (0.035 M), was dissolved in 50 ml. of 95% ethanol. To this solution was added anhydrous hydrazine, 0.570 g. (0.018 M). The ethanolic solution was heated at reflux for five minutes on a steam bath and then allowed to cool. The crystalline product was collected by suction filtration from the cold ethanol and washed several times with water. The resulting yellow solid was dried in a vacuum oven at 110°C. The yield was essentially quantitative. The observed m.p. was 212-213°C; literature[7] 211°C.

2. (DA-39-104) Synthesis of p-Xylilidine-4,4'-dichloroanil.

Terephthaldehyde, 10.00 g. (0.074 M), was dissolved in 125 ml. of boiling benzene in a flask fitted with a Dean-Stark apparatus, a magnetic stirrer, and a nitrogen inlet. To this solution was added p-chloroaniline, 19.00 g. (0.148 M). The reaction proceeded until the theoretical amount of water was collected in the trap. The benzene was then evaporated to leave a yellow solid which was recrystallized from 95% ethanol. The yield was essentially quantitative. The observed m.p. was 180-181°C.

Analysis:[8] Calc'd for $C_{20}H_{14}Cl_2N_2$: C, 68.00; H, 3.99; Cl, 20.07; N, 7.93.

Found: C, 67.98; H, 4.02; Cl, 20.11; N, 7.91.

3. (DA-39-124) Synthesis of Perfluorobenzalazine.

Pentafluorobenzaldehyde, 2.00 g. (0.010 M), and hydrazine hydrate 85% in water, 0.36 g. (0.005 M) were both dissolved in 30 ml. of refluxing benzene in a flask equipped with a Dean-Stark apparatus, magnetic stirrer, and nitrogen inlet. The reaction was allowed to continue until the theoretical amount of water had been collected. The benzene was then evaporated and the yellow product recrystallized from 95% ethanol. The yield was essentially quantitative. The observed m.p. was 139-140°C.

Analysis:[9] Calc'd for $C_{14}H_2F_{10}N_2$: C, 43.31; H, 0.52; F, 48.95; N, 7.22.

Found: C, 43.09; H, 0.79; F, 48.99; N, 7.42.

4. (DA-39-125) Synthesis of p-Xylilidenediperfluoroanil.

Terephthaldehyde, 1.46 g. (0.011 M), and pentafluoroaniline, 4.00 g. (0.022 M) were mixed in 25 ml. of refluxing benzene in a flask equipped with a Dean-Stark apparatus, magnetic stirrer, and a nitrogen inlet. The reaction was catalyzed by a small amount of zinc chloride. The reaction was continued until the theoretical amount of water was collected in the trap. The benzene was evaporated and the solid obtained was recrystallized from benzene. The yield obtained was 90% of the theoretical. The observed m.p. was 207-208°C.

Analysis:[9] Calc'd for $C_{20}H_6F_{10}N_2$: C, 51.74; H, 1.30; F, 40.92; N, 6.04.

Found: C, 51.71; H, 1.27; F, 40.84; N, 6.28.

5. (DA-39-126) Synthesis of 4,4'-Difluorobenzalazine.

p-Fluorobenzaldehyde, 3.00 g. (0.024 M), and hydrazine hydrate 85% in water, 0.71 g (0.012 M), were added to 30 ml. of refluxing benzene in a flask

equipped with a Dean-Stark apparatus, a magnetic stirrer, and a nitrogen inlet. The reaction was stopped when the theoretical amount of water had been collected. The benzene was evaporated and the resulting solid recrystallized out of benzene. The yield obtained was 93%. The observed m.p. was 188.5-189.5°C.

Analysis:[9] Calc'd for $C_{14}H_{10}F_2N_2$: C, 68.84; H, 4.13; F, 15.59; N, 11.47.

Found: C,69.07; H, 4.43; F, 15.72; N, 11.45.

6. (DA-46-25) Synthesis of p-Xylilidene-p-difluorodianil.

p-Fluoroaniline, 11.10 g. (0.100 M), and terephthaldehyde, 6.70 g. (0.050 M) were mixed in 180 cc. of refluxing benzene in a flask equipped with a Dean-Stark apparatus, a magnetic stirrer, and a nitrogen inlet. After about eighteen hours of refluxing, the calculated amount of water was collected in the trap and the reaction ceased. The solution was filtered hot and the filtrate then allowed to crystallize. The yield was essentially quantitative. The observed m.p. was 153-154°C.

Analysis:[9] Calc'd for $C_{20}H_{14}F_2N_2$: C, 74.85; H, 4.41; F, 11.91; N, 8.81.

Found: C, 74.55; H, 4.27; F, 12.32; N, 8.82.

III. Syntheses of Polymers.

In the previous reports[1,2] it had been demonstrated that the bis-exchange method as exemplified by equation 2 was the best method of polyazine synthesis:

$$n\ C_6H_5CH{=}N\text{-}N{=}HCC_6H_5 + n\ C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5 \xrightarrow[N_2]{\Delta}$$

$$\rightarrow \left[HCC_6H_4CH{=}N\text{-}N{=}\right]_n + 2n\ C_6H_5CH{=}NC_6H_5 \qquad \text{(eq. 2)}$$

This method was shown to produce black, infusible, high molecular weight polyazine polymers which possessed excellent thermal stability. In an attempt to produce such a thermally stable polymer more directly in a single step, a synthesis was carried out employing the four reagent com-

pounds: benzaldehyde, hydrazine, terephthaldehyde and aniline.

It was also considered desirable to synthesize a black polyazine by the bis-exchange method which contained fluorine end-groups for subsequent use in molecular weight determinations in those cases where the polymer had been exposed to elevated temperatures.

A. Experimental.

1. (DA-39-139) Synthesis of Fluorine Tagged Black Polymer.

Perfluorobenzalazine, 0.4938 g. (1.27×10^{-3} M), and p-xylilideneperfluorodianil, 0.5905 g. (1.27×10^{-3} M), were mixed in a tube equipped with a side arm. The tube was placed in a heating block and maintained at 230°C. The melt gradually darkened in color and grew more viscous. After twenty hours the pressure was reduced to 2.5 mm Hg and kept there for twenty-four hours. The reaction was then stopped and a black, glassy polymer recovered.

2. (DA-39-137-A) Direct Synthesis of Polyazine.

Benzaldehyde, 1.000 g. (9.00×10^{-3} M) and terephthaldehyde, 0.461 g. (3.00×10^{-3} M) were added to a microflask in an inert atmosphere of nitrogen. To this was added a mixture of 0.6406 g. (6.90×10^{-3} M) aniline (freshly distilled), and 0.1900 g. (4.70×10^{-3} M) hydrazine (85% in water). The mixture became exothermic with the formation of a pasty yellow solid. The temperature was raised gradually to 230°C over a one-hour period during which time the yellow solid eventually melted and a dark liquid resulted. The temperature was raised to 250°C and held there for twenty-four hours, during which time the liquid increased in viscosity, and darkened in color. After twenty-four hours the microflask was equipped for distillation and the pressure reduced to 1.5 mm Hg for sixteen hours. Some by-product appeared in the distillation head and a glassy, black polymer was recovered.

3. (DA-39-137-B) Thermal Evaluation of Direct Synthesis of Polymer DA-39-137.

The black, glassy, infusible polymer obtained from the one-step direct synthesis method was evaluated for thermal stability by means of thermal Gravimetric Analysis (TGA). The thermogram for this polymer is shown in Appendix No. 1. Trace A represents the weight loss incurred when the sample was heated initially in a nitrogen atmosphere at 15°C per minute. Trace B represents the weight loss curve obtained when the polymer, previously heated to 1176°C in nirrogen, was then cooled and reheated at 15°C per minute in air.

B. Discussion.

The results of the two previous experiments indicate that it is possible to obtain a thermally stable, high molecular weight, black polyazine by a direct reaction of the constituent reagent compounds. This conclusion is justified by examining the TGA thermogram of this polymer (Appendix No. 1). Its traces are quite similar to those of black, high molecular weight polyazines obtained by the method of bis-exchange employing appropriate derivatives of the reagent compounds as shown in Appendix No. 2. It is probable that the hydrazine, being inherently more reactive than the aniline, reacts first with the two aldehydes forming several possible Schiff-base compounds and oligomers. The aniline then most probably reacts with the remaining benzaldehyde and residual terephthaldehyde to form additional Schiff-base compounds which can then react in a bis-exchange reaction yielding the desired polymer. This method of synthesis obviates the necessity of preparing and purifying the derivative compounds necessary for the bis-exchange.

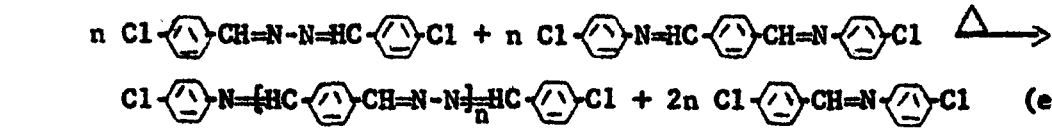
The synthesis of the fluorine-tagged polymer proceeded in much the same fashion as the untagged with the exception that the tagged polymer

appeared to be much more soluble than the untagged variety.

IV. Attempts to Determine Molecular Weights of Black Azine Polymers.

In a previous report[2] the approximate molecular weight of a low molecular weight, yellow azine polymer, prepared by direct condensation in solution, was determined to be about 700, corresponding roughly to a tetramer. This assignment was made on the basis of infrared spectroscopy and elemental analysis. It is desirable to have also some reliable estimate of the molecular weight of the corresponding black azine polymers obtained by the melt techniques. Most conventional means of molecular weight determination were not applicable due to the very limited solubility of these polymers, that is, they are essentially insoluble in all solvents except strong acids, which most likely degrade them. Thus it became necessary to attempt other methods. One method which was believed to be applicable was that of end group tagging and subsequent analysis for the presence of the end group in the final polymer. It had also been observed in previous experiments that as polymerization proceeded a distinct color sequence was noted. The initial melt solutions were invariably yellow in color, and as the reaction proceeded the viscosity of the melt increased predictably as the molecular weight also increased. Also, the color of the melt changed from the initial yellow to orange, red, brown and eventually to black. The final transformation involved the bubbling of the very viscous black melt and eventual solidification. It was hoped, therefore, to determine the molecular weights of the polymer at each general color stage in the reaction by the previously mentioned method of tagging and analysis, and to obtain some correlation of observed color with approximate molecular weight. The end groups decided upon were aromatic halogens, specifically chlorine and fluorine. Fluorine,

being more thermally stable, was the end group of choice when elevated temperatures were involved in the polymerization. The method of analysis chosen was elemental analysis by a professional analyzing service. This particular method lends itself to the polyazine since the method of synthesis, that is, the bis-exchange, is uniquely suited for the placing of desired end groups on the polymer. An example of such a reaction is seen in equation 3.



(eq. 3)

Also it was believed that a purification process could be developed for the polymers since the entrapped by-product and any unreacted monomer could be removed by extensive extraction with a suitable solvent, that is, one in which the undesirable products were soluble and the polymer insoluble.

A. Experimental.

1. (DA-39-105-A) Synthesis of Low Molecular Weight Yellow Melt Polyazine.

2,2'-Dichlorobenzalazine, 1.0015 g. (0.0036 M), and p-xylilidene 4,4'-dichlorodianil, 1.2628 g. (0.0036 M) were placed in a reaction tube equipped with a side arm and a condenser along with a nitrogen gas inlet for an inert atmosphere. The two solids were heated to 225°C and the resulting melt kept at that temperature for forty-eight hours. The reaction was stopped when a yellow solid button of material was in evidence at the bottom of the tube. The polymer was then prepared for extraction by being ground to a fine powder by shaking in a steel capsule for one minute.

2. (DA-39-105-B) Extraction of DA-39-105-A.

The yellow solid, DA-39-105, 0.1466 g., was placed in a micro Soxhlet extraction apparatus and extracted for twenty-four hours with 95% ethanol.

At the end of this time the filtrate was clear and gave a negative Beilstein copper wire test for the presence of halogen as compared to a known positive sample. The polymer was then recovered, dried in a vacuum oven at 110°C for several hours. The weight loss of polymer in the extraction amounted to 34.80% and this material was recovered upon evaporation of the filtrate. The recovered material had a broad melting point, 80-100°C, and its infrared spectrum, Appendix No. 3, appeared to indicate that it was a mixture of by-product, unreacted monomer and some low molecular weight oligomer.

3. (DA-39-108-A) Synthesis of Low Molecular Weight Orange Melt Polyazine.

4,4'-Dichlorobenzalazine, 0.9798 g. (0.0035 M), and p-xylilidene 4,4'-dichlorodianil, 1.2352 g. (0.0035 M) were mixed in a reaction tube equipped with a side arm and condenser along with a nitrogen gas inlet for an inert atmosphere. The two solids were heated to 240°C and kept there for twenty-four hours. The reaction was stopped and an orange button was then recovered. The polymer was prepared for extraction by being ground to a fine powder by shaking in a steel capsule for one minute.

4. (DA-39-108-B) Extraction of DA-39-108-A.

The orange solid, DA-39-108-A, 0.1125 g., was placed in a micro Soxhlet extraction apparatus and extracted for twenty-four hours with 95% ethanol. At the end of this time the filtrate was clear and gave a negative Beilstein test for halogen. The recovered polymer was then dried in a vacuum oven at 110°C for three hours. The weight loss of the polymer in the extraction amounted to 70.76% and this material was recovered upon evaporation of the filtrate. Again the recovered material had a broad melting point, 80-100°C, and its infrared spectrum, Appendix No. 4, appears identical to that obtained from DA-39-105.

5. (DA-39-110-A) Synthesis of a Brown Polyazine.

4,4'-Dichlorobenzalazine, 0.5055 g. (0.0018 M) and p-xylilidene 4,4'-dichlorodianil, 0.6373 g. (0.0018 M) were treated as in DA-39-108-A with the exception that the temperature was raised and held at 255°C for twenty-four hours. The reaction was stopped when an orange-brown button was obtained in the reaction tube. This polymer was prepared for extraction by being ground in a steel capsule for one minute.

6. (DA-39-112-B) Extraction of DA-39-110-A.

The orange-brown solid, DA-39-110-A, 0.0978 g., was extracted as in DA-39-108-B with 95% ethanol. The weight loss of the polymer in the extraction amounted to 60.22% and this material was recovered upon evaporation of the filtrate. The recovered material again exhibited a very broad melting range, 80-100°C, and its infrared spectrum, Appendix No. 5, is quite similar to those obtained from extraction of the two previous polymers.

7. (DA-39-117-A) Synthesis of a Black Fusible Polyazine.

4,4'-Dichlorobenzalazine, 0.5314 g. (0.0019 M) and p-xylilidene 4,4'-dichlorodianil, 0.6732 g. (0.0019 M) were placed in a reaction tube in an inert atmosphere. The tube was placed in a heating block and the temperature slowly raised to 290°C and held there for seven hours. At that point a very dark, viscous melt was in evidence. The tube was then cooled and a black, solid polymer obtained. This polymer was prepared for extraction by being ground in a steel capsule for one minute.

8. (DA-39-117-B) Extraction of DA-39-117-A.

The dark-brown solid, DA-39-117-A, 0.1067 g., was extracted as in DA-39-110-B with 95% ethanol. The weight loss of the polymer in the ex-

traction amounted to 47.72% and this material was recovered upon evaporation of the filtrate. The recovered material had a broad melting range, 80-100°C, and its infrared spectrum, Appendix No. 6, again appears similar to those obtained from polymers mentioned previously.

9. (DA-39-118-A) Synthesis of Black, Infusible Polyazine.

4,4'-Dichlorobenzalazine, 0.5592 g. (0.0020 M) and p-xylilidene 4,4'-dichlorodianil, 0.7051 g. (0.0020 M) were reacted in a similar manner. The temperature was raised to 290°C and held there for thirteen hours, after which time a black button was recovered. This was then ground in a steel capsule for one minute and extracted.

10. (DA-39-118-B) Extraction of DA-39-118-A.

The black solid, DA-39-118-A, 0.1204 g., was extracted as in DA-39-112-B with 95% ethanol. The weight loss of the polymer in the extraction amounted to 42.21% and this material was recovered upon evaporation of the filtrate. The recovered material had a broad melting range, 80-100°C, and its infrared spectrum, Appendix No. 7, is very similar to the melting points and infrared spectra obtained from extraction of those polymers examined previously.

11. (DA-39-120-A) Synthesis of Black, Infusible Polyazine.

4,4'-Dichlorobenzalazine, 0.4978 g. (0.0018 M) and p-xylilidene 4,4'-dichlorodianil, 0.6251 g. (0.0018 M) were placed in a reaction tube equipped wirh a nitrogen inlet, a side arm and a condenser. The mixture was placed in a heating block and heated to 290°C and held there for thirteen hours. Then the pressure was reduced to 2 mm Hg and held there for three hours. When the reaction was completed a black, infusible button was obtained. This was ground in a steel capsule for one minute and then extracted.

12. (DA-39-120-B) Extraction of DA-39-120-A.

The black solid, DA-39-120-A, 0.0976 g., was extracted as in DA-39-118-B

with 95% ethanol. The weight loss of the polymer was 8.72% in the extraction. This material was not recovered.

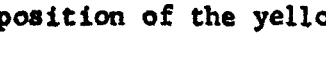
B. Discussion.

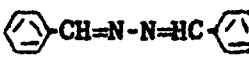
At the present time work is continuing on this aspect of determining molecular weights. The polymers prepared thus far and extracted will be subsequently analyzed for the presence of the halogen as well as for the other elements. If this method proves reliable it should then be possible to obtain an estimate of the kinetics of the Schiff base bis-exchange condensation reaction employed in the polyazine synthesis by similar procedures. The hope is that the polymerizations could be carried out isothermally for varying intervals of time, producing polymers whose molecular weight, as determined from end group analyses, would increase with time. From the increasing molecular weight and corresponding $\overline{DP}$ (average degree of polymerization) it would be possible to relate[10] the extent of reaction (p) with time in a kinetic plot, knowing

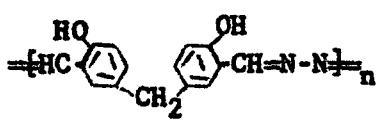
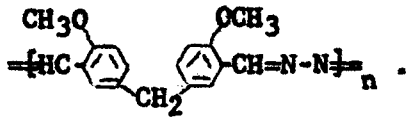
$$\overline{DP} = 1/1-p \ .$$

It should also be pointed out again that, as was found in synthesizing the fluorine-tagged polyazine, the chlorine-tagged polymer evidenced a somewhat greater solubility in the melt phase than the unsubstituted polyazines. This solubilizing factor is evidently due to the steric and/or electronic effects of the ring-substituted halogen.

V. Kinetic Studies on Decomposition of Yellow Polyazines Using the Method of Freeman and Carroll.[5]

In a previous report[2] the method of Freeman and Carroll[5] employing measurements of slopes of polymer decomposition thermogravimetric analysis (TGA) traces, was used to give the order of reaction and energy of activation for the decomposition of the yellow polyazine, 

prepared by the solution method. The reaction was calculated as first order and the energy of activation obtained, 27.4 kcal/mole. The decomposition reaction of the monomer, benzalazine,  , was determined as first order[11] and its activation energy as 53 kcal/mole. In order to assess the effect of substituents and particularly hydrogen bonding on the decomposition, the same method of Freeman and Carroll was applied to the yellow solution-prepared polymers:

 and  .

Briefly, the method of Freeman and Carroll is based on the following derived expression by Anderson and Freeman.[12]

$$\Delta \log (dw/dt) = x \Delta \log W_r - (\Delta E^*/2.3\ R)\Delta(1/T) \qquad \text{(eq. 4)}$$

where: dw/dt = the rate of reaction

x = the order of reaction

ΔE^* = the energy of activation

R = the gas constant

T = the absolute temperature

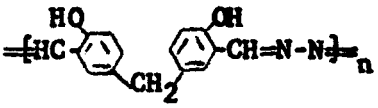
W_r = $W_c - W$ (proportional to the amount of reactant)

ΔW = the weight loss at the point where dw/dt is taken

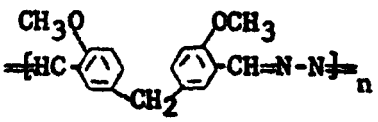
ΔW_c = the total weight loss associated with a given reaction

To evaluate the constants in equation 4, $\Delta \log dw/dt$ is plotted against $\log W_r$ if $\Delta(1/T)$ is kept constant. The order of reaction, x, is determined from the slope and the energy of activation from the intercept of $\Delta \log W_r = 0$. A simple method of determining dw/dt and W_r at constant $\Delta(1/T)$ is to plot the first derivatives of the primary thermogravimetric curve and corresponding W_r as a function of reciprocal absolute temperature.

A. Experimental.

1. Thermogravimetric Analysis of Polymer DA-39-93, 

Appendix No. 8 shows the TGA trace of DA-39-93. The heating rate was 5°C/minute for a 9.87 mg. sample in an inert atmosphere of nitrogen. Appendix No. 9 shows the plot of the first derivative of the TGA curve as well as W_r for the sample as a function of reciprocal absolute temperature. Appendix No. 10 shows the plot of $\triangle$ log dw/dt as a function of $\triangle$ log W_r.

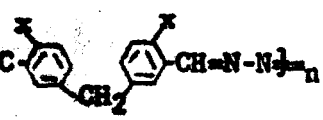
2. Thermogravimetric Analysis of Polymer DA-39-95, 

Appendix No. 11 shows the TGA trace for DA-39-95. The heating rate was 5°C/minute for a 9.93 mg. sample in an inert atmosphere of nitrogen. Appendix No. 12 shows the plot of the first derivative of the TGA curve as well as W_r for the sample as a function of reciprocal absolute temperature. Appendix No. 13 shows the plot of $\triangle$ log dw/dt as a function of $\triangle$ log W_r.

B. Calculations.

As was mentioned previously, the energy of activation ($\triangle E^*$) and the order of reaction (x) are calculated using the following derived equation:

$$\triangle \log (dw/dt) = x \triangle \log W_r - (\triangle E^*/2.3\ R) \triangle (1/T). \qquad \text{(eq. 5)}$$

These unknowns can be obtained for DA-39-93, x = OH, and for DA-39-95, x = OCH_3,  , respectively by a consideration of the plots in Appendix No. 10 and Appendix No. 13.

1. Calculation for DA-39-93.

Using the data from Appendix No. 10 to obtain $\triangle$ log (dw/dt) (intercept at $\triangle$ log W_r = 0) and substituting into equation 5:

$$-5.62 \times 10^{-2} = x\cancel{\Delta \log^{\circ} W_r} - \frac{\Delta E^*}{(2.3)(1.99)} \cdot \left(-\frac{0.5 \times 10^{-5}}{^\circ K}\right)$$

$$\Delta E^* = 52 \text{ kcal/mole.}$$

Calculation of the slope of the line in Appendix No. 10 gives a reaction order (x) of 1.29.

2. Calculation for DA-39-95.

Utilizing the data from Appendix No. 13 to obtain $\Delta \log dw/dt$ (intercept at $\Delta \log W_r = 0$) and substituting into equation 5:

$$-4.5 \times 10^{-2} = x\cancel{\Delta \log^{\circ} W_r} - \frac{\Delta E^*}{(2.3)(1.99)} \cdot \left(-\frac{0.5 \times 10^{-5}}{^\circ K}\right)$$

$$\Delta E^* = 41 \text{ kcal/mole.}$$

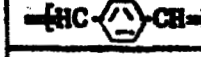
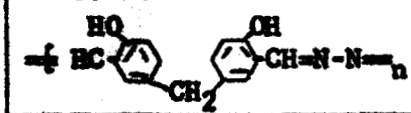
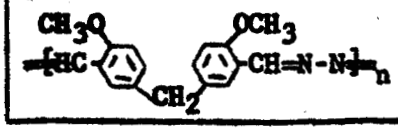
Calculation of the slope of the line in Appendix No. 13 yields a reaction order (x) of 1.32.

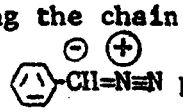
C. Discussion.

At this point we can sum up the results that have been obtained for the three yellow polyazines employing the method of Freeman and Carroll to monitor their decomposition.

Table 1

Parameters for Polyazine Decomposition

Polymer	Order Reaction	Energy of Activation
DA-39-94 	1.08	25 kcal/mole
DA-39-93 	1.29	52 kcal/mole
DA-39-95 	1.32	41 kcal/mole

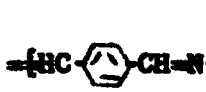
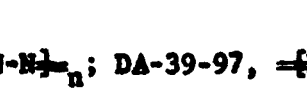
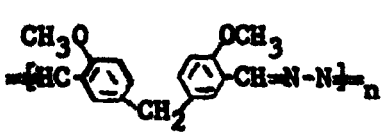
From this data it appears that the polymer decomposition is essentially first order as was found previously to be the case for the azine monomer decomposition. The order of the activation energies is what might have been expected. The hydroxy polymer DA-39-93 requires the greatest activation energy due to the presence of hydrogen bonding between the azine nitrogen and the phenolic hydrogen. The methoxy polymer DA-39-95 requires the next greatest activation energy due to both the bulk factor resulting from the $-OCH_3$ groups in shielding the chain from attack by the probable decomposition chain-carrying species,  phenyldiazomethane, and also due to the residual hydrogen bonding resulting from the OCH_2-H---N. The unsubstituted polymer, DA-39-34, requires the lowest energy of activation in this series. The order of magnitude for the energies of activation also parallels that of the temperatures required for decomposition of the monomers, that is, $-OH > -OCH_3 >$ unsubstituted.

VI. Kinetic Studies on Decomposition of Black Polyazines Using the Method of Freeman and Carroll.[5]

The method of Freeman and Carroll[5] has provided some information concerning decomposition as observed in the low molecular weight yellow polyazines. It was therefore decided to attempt to apply this method to the decomposition of the black polyazines.

A. Experimental.

1. Thermogravimetric Analyses of Black Polyazines.

Appendices Nos. 14, 15, and 16 show the thermogram traces of DA-39-43,  ; DA-39-97,  ; and DA-39-99,  respectively. All were run in a nitrogen atmosphere at a heating rate of 5°C/minute.

2. Differential Thermal Analyses of Black Polyazines.

Appendices Nos. 17, 18 and 19 show the differential thermal analysis (DTA) traces for DA-39-43, DA-39-97 and DA-39-99 respectively. All were run in a nitrogen atmosphere at a heating rate of 15°C/minute.

B. Discussion.

An examination of the TGA thermograms for these black polymers reveals the traces for the weight loss to be somewhat different from those obtained from the corresponding yellow polymers under the same conditions. While the slopes for the thermograms of the black polymers are smooth and continual, those of the yellow polymers are broken with shoulders reflecting the beginning and end of the decomposition. Even more striking are the differences in the DTA thermograms for the yellow and black samples. The DTA thermograms for the yellow polymers exhibit strong exothermic peaks very near the temperatures of maximum rate of weight loss as given by the TGA, as shown in the previous report.[2] The black polymers, however, do not reveal such sharp exotherms in their DTA thermograms but rather have relatively broad exotherms which smoothly trail off at elevated temperatures actually having no maximum. Such data seem to suggest that weight loss processes in the two types of polymers are not quite the same. The major weight losses for the yellow polymers at temperatures up to 400 or 450°C seem to be due mainly to the nitrogen decomposition as indicated by their TGA and DTA thermograms. However, the black polymers appear to have weight losses due to other factors besides nitrogen decomposition. Such factors may include diffusion and vaporization of by-product, which predominate in the TGA, giving a trace of continual and smooth weight loss, and in the DTA giving a corresponding broad diffused exotherm. Such results, therefore, must preclude any application of the

method of Freeman and Carroll[5] to these polymers in attempt to monitor nitrogen decomposition, because of the complicating factor of the vaporization of the occluded by-product. The yellow polymers prepared by the solution method do not contain any occluded by-product which does result from the Schiff base bis-exchange condensation syntheses of polyazines.

VII. Kinetic Data on Decomposition of Yellow Polyazines Using the Method of Flynn and Wall.[6]

A recent method for the simple and quick determination of the activation energy of a polymer decomposition has been introduced by Flynn and Wall.[6] This method for determining the activation energy from TGA plots involves only the reading of the temperature at a constant weight loss from several integral thermograms at different heating rates. An equation is derived by Flynn and Wall, which is the basis for the determinations, relating the energy of activation with the heating rates and corresponding temperatures of constant weight loss.

$$E \cong -4.35 \, d \log \beta / d \, 1/T \qquad \text{(eq. 6)}$$

where

T = absolute temperature corresponding to constant weight loss

β = constant heating rate

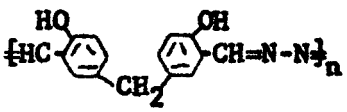
E = energy of activation

Then, from the slope of a plot of log β versus 1/T at a particular constant weight loss, the activation energy may be calculated. This method was employed with the three polyazines previously tested by the method of Freeman and Carroll.[5]

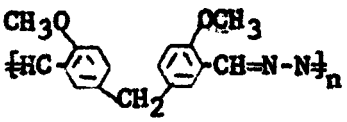
A. Experimental.

1. Thermogravimetric Analysis of Polymer DA-39-34,  , Employing Different Heating Rates.

Appendix No. 20 shows the decomposition of the yellow azine polymer, DA-39-34, in nitrogen. Lines 1, 2 and 3 represent heating rates of 5, 10 and 15°C per minute respectively, at constant weight losses corresponding to A, B and C on Appendices Nos. 20 and 21. Appendix No. 21 shows the plot of log β (heating rate) versus 1/T· (°K).

2. Thermogravimetric Analysis of Polymer DA-39-93,  , Employing Different Heating Rates.

Appendix No. 22 shows the decomposition of the yellow azine polymer, DA-39-93, in nitrogen. Lines 1, 2 and 3 represent heating rates of 5, 10 and 25°C per minute respectively at constant weight losses corresponding to A, B and C on Appendices Nos. 22 and 23. Appendix No. 23 shows the plot of log β (heating rate) versus 1/T· (°K).

3. Thermogravimetric Analysis of Polymer DA-39-95,  , Employing Different Heating Rates.

Appendix No. 24 shows the decomposition of the yellow azine polymer, DA-39-95, in nitrogen. Lines 1, 2 and 3 represent heating rates of 10, 15 and 30°C per minute respectively at constant weight losses corresponding to A, B and C on Appendices Nos. 24 and 25. Appendix No. 25 shows the plot of log β (heating rate) versus 1/T (°K).

B. Calculations.

1. For Polymer DA-39-34.

Utilizing Appendix No. 21 to calculate log β/ 1/T (slope), E, the activation energy can be calculated by substitution in equation 6:

$$E = -4.35 \, d \log \beta / d \, 1/T$$

$$E = -4.35 \cdot (-8.5)$$

$$E = 37 \text{ kcal/mole.}$$

The slope used is the average of the three in Appendix No. 21.

2. For Polymer DA-39-93.

Utilizing Appendix No. 23 to calculate log β/ 1/T (slope), E, the activation energy can be calculated by substitution in equation 6:

$$E = -4.35 \, d \log \beta / d \, 1/T$$

$$E = -4.35 \cdot (-15.4)$$

$$E = 67 \text{ kcal/mole.}$$

The slope used is the average of the three in Appendix No. 23.

3. For Polymer DA-39-95.

Utilizing Appendix No. 25 to calculate log β/ 1/T (slope), E, the activation energy can be calculated by substitution in equation 6:

$$E = -4.35 \, d \log \beta / d \, 1/T$$

$$E = -4.35 \cdot (-12.6)$$

$$E = 55 \text{ kcal/mole.}$$

The slope used again is the average of the three in Appendix No. 25.

C. Discussion.

Table 2 is a summary of the results obtained on the polymer decomposition activation energies obtained by the methods of Flynn and Wall[6] (FW) and Freeman and Carroll[5] (FC).

Table 2

The Order and Activation Energy
of the Decomposition of Azine Polymers

Polymer	Order (FC)	E_a (FC) kcal/mole	E_a (FW) kcal/mole	E_a kcal/mole
DA-39-34	1.08	25	37	+ 12
DA-39-93	1.29	52	67	+ 15
DA-39-95	1.32	41	55	+ 14

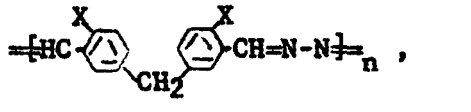
The results obtained from the method of Flynn and Wall[6] give activation energies which are uniformly 12 to 15 kcal/mole greater than those obtained by the Freeman and Carroll[5] method. The reason for this discrepancy is not clear at this time.

VIII. Summary and Conclusions.

(1) A direct one-step method for synthesizing black high molecular weight polyazines was demonstrated.

(2) Several new fluorine and chlorine containing azine and Schiff base monomers were synthesized and characterized by elemental analysis.

(3) Preliminary attempts were initiated in order to determine the approximate molecular weights of the black azine polymers. The method of end group analysis was selected and tagging of the polymer ends was accomplished with chlorine and fluorine moieties via the Schiff base bis-exchange reaction. The polymers so tagged will next be analyzed for the presence of the chlorine or fluorine.

(4) The method of Freeman and Carroll was used to monitor the decomposition of two yellow azine polymers;  , where X = OH and OCH_3 to yield its order of reaction and energy of activation.

(5) This same method of evaluation was found not to be applicable to the decomposition of the black azine polymers due to the incorporation of by-products.

(6) A recent method devised by Flynn and Wall which yields the activation energies for polymer decomposition was applied to the yellow azine polymer decomposition.

IX. References.

1. G.F. D'Alelio and R. Schoenig, "Fundamental Studies on the Synthesis of Heat-Resistant Polymers," Preliminary Studies on the Synthesis of Polymeric Azines, Report No. 8 under NASA Grant NsG339, September 15, 1965.

2. G.F. D'Alelio and R. Schoenig, "Fundamental Studies on the Synthesis of Heat-Resistant Polymers," The Synthesis and Evaluation of Polymeric Azines, Report No. 10 under NASA Grant NsG339, February 15, 1966.

3. T. Curtius and R. Jay, J. prakt. Chem., [2], 39, 45 (1889).

4. H. Zimmerman and S. Somasekhara, J. Am. Chem. Soc., 82, 5865 (1960).

5. E. Freeman and B. Carroll, J. Phys. Chem., 62, 394 (1958).

6. J. Flynn and L. Wall, Polymer Letters, 4, 323 (1966).

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8. Midwest Microlab, Inc., 6000 East 46th St., Indianapolis, Indiana.

9. Schwarzkopf Microanalytical Lab., 56-19 37th Avenue, Woodside, New York.

10. P.J. Flory, J. Am. Chem. Soc., 58, 1877 (1936).

11. G. Williams and A. Lawrence, Proc. Roy. Soc. (London), 156A, 444 (1936).

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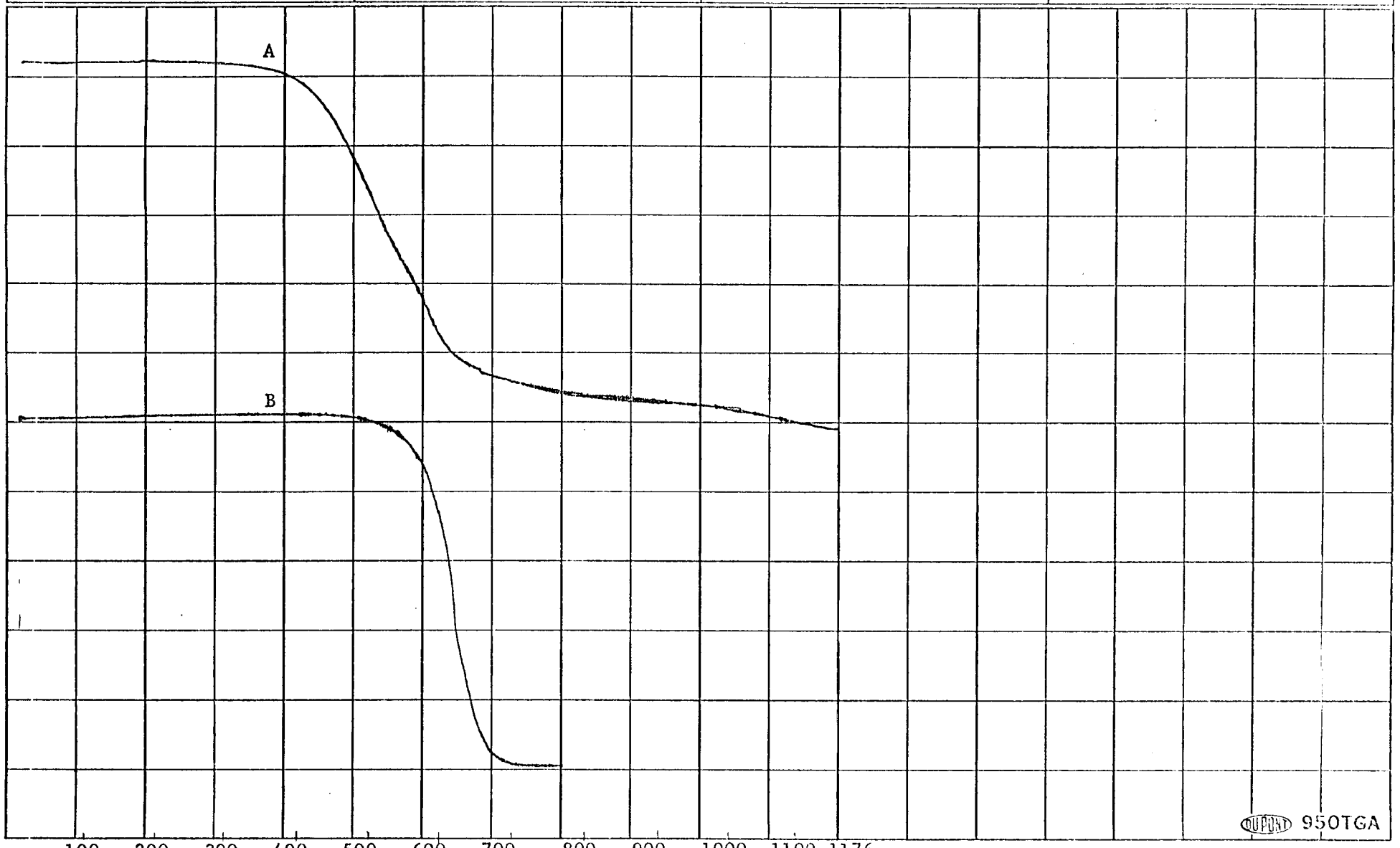
WILMINGTON 98, DELAWARE

SAMPLE: DA-39-137	X-AXIS	Y-AXIS	RUN NO. ____ DATE ____
$=\left[HC\text{-}\langle\rangle\text{-}CH{=}N\text{-}N\right]_n=$	TEMP. SCALE 200 °C / inch	SCALE 2 mg. / inch	OPERATOR RKS
Black	SHIFT 0 inch	(SCALE SETTING X 2)	HEATING RATE 15 °C / min.
SIZE 10.35 mg.	TIME SCALE (ALT.) 0	SUPPRESSION 0 mg.	ATM. a) N_2; b) air
			TIME CONSTANT 2 sec.



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

Appendix No. 1

PART NO. 950017

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

SAMPLE: DA-39-80

Black

SIZE 9.82 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.

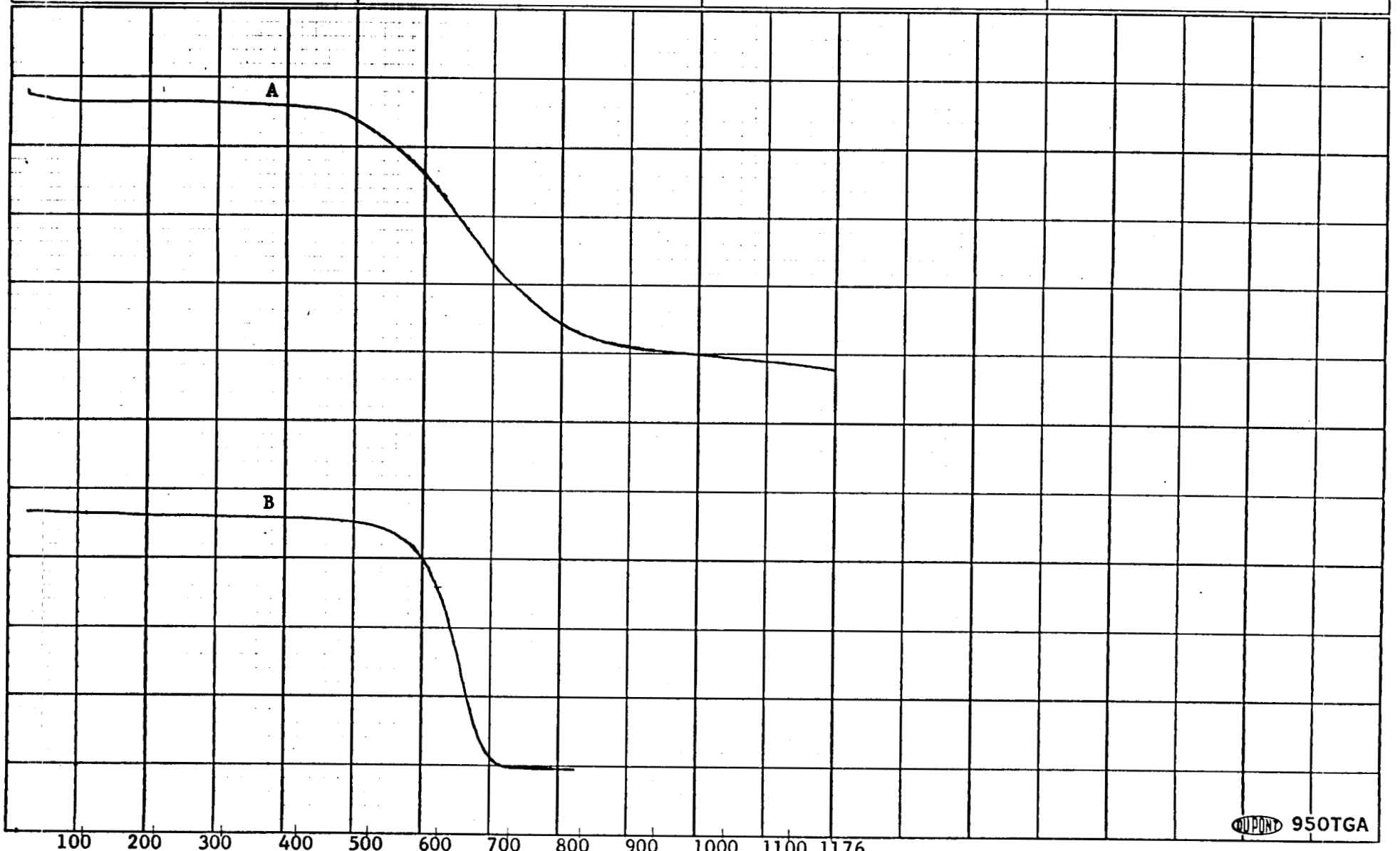
RUN NO. _____ **DATE** _____

OPERATOR RKS

HEATING RATE 15 °C / min.

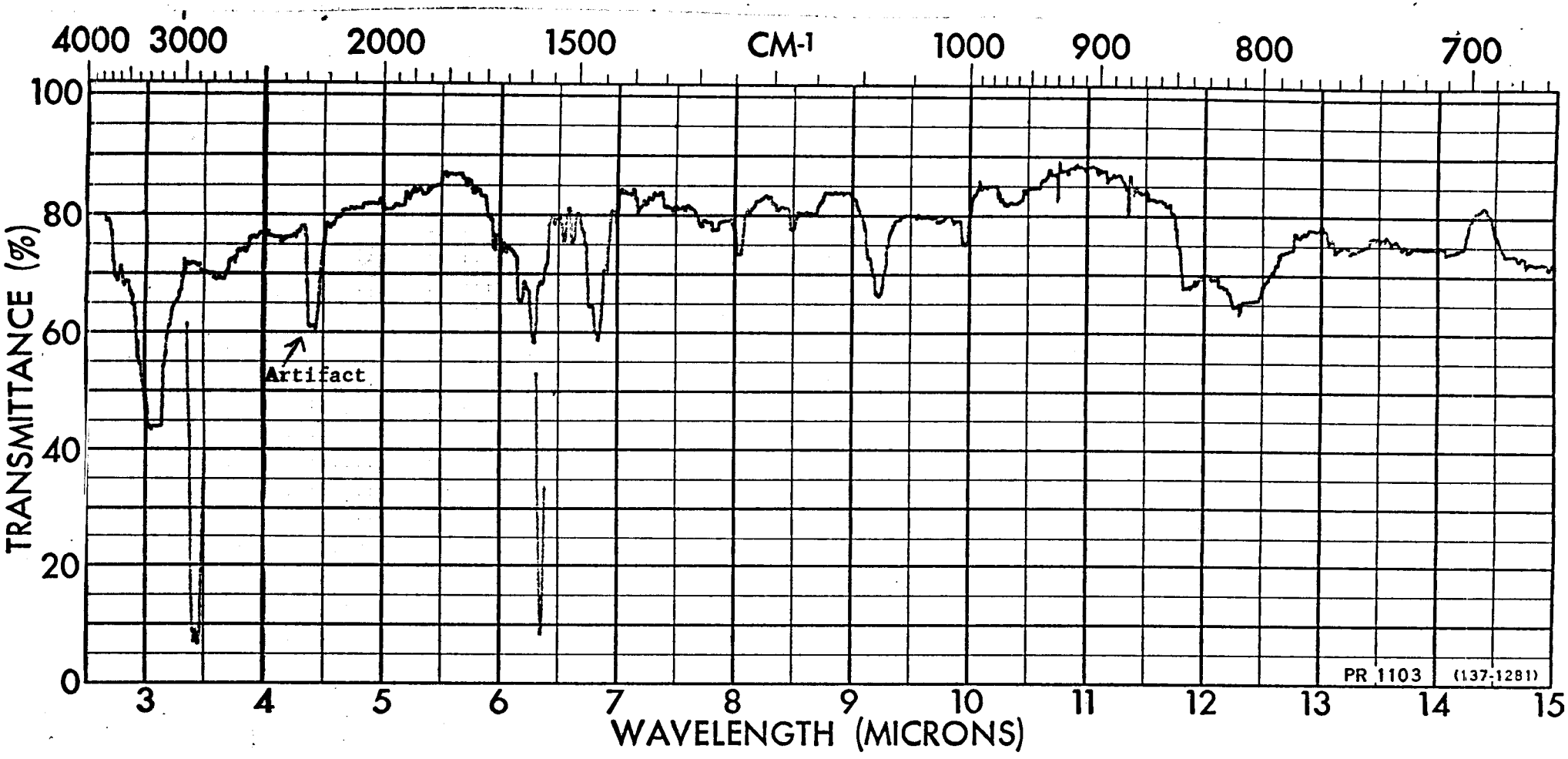
ATM. a) N_2; b) air

TIME CONSTANT 2 sec.



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

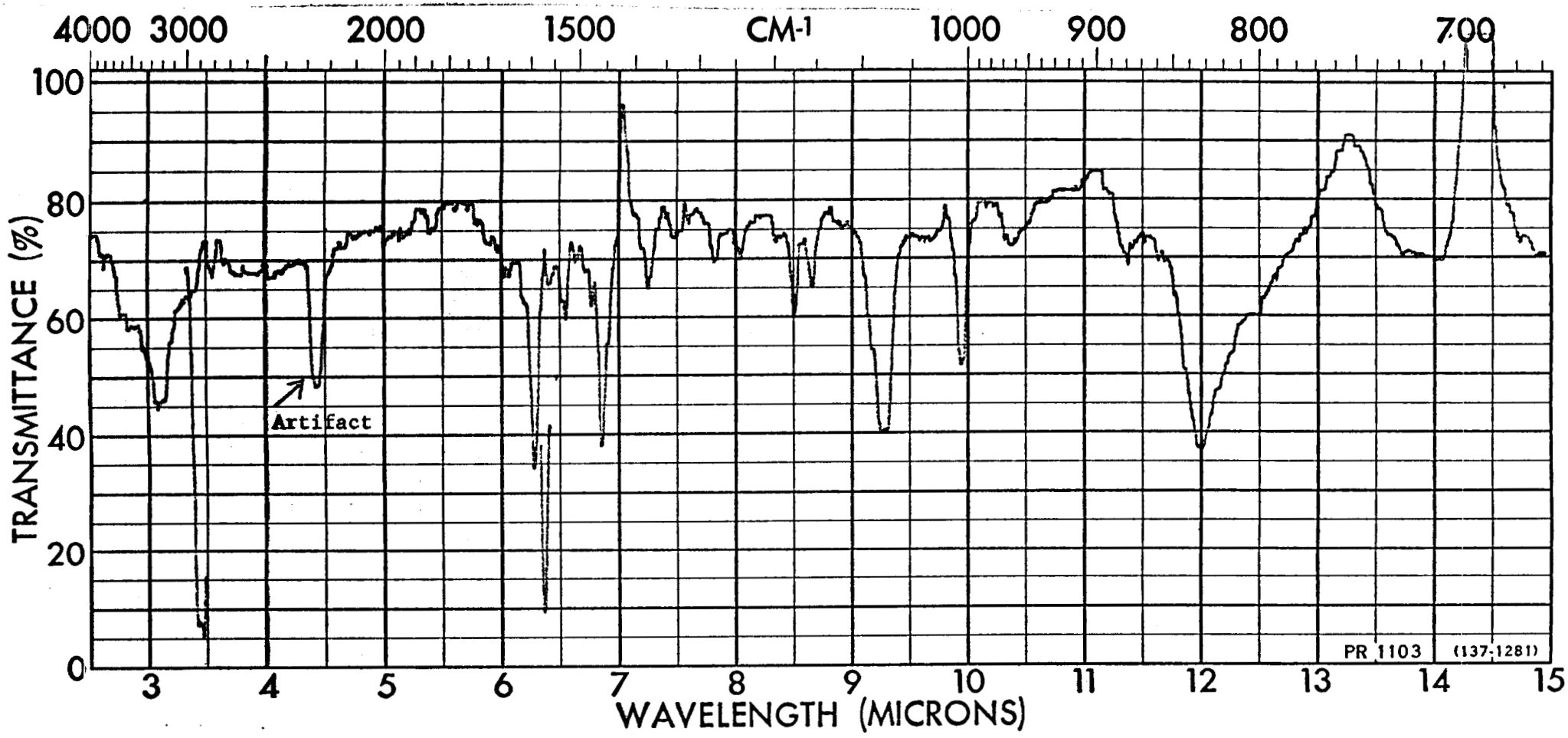
Appendix No. 2



KBr Disc

Solid from Filtrate of EtOH Extraction of DA-39-105

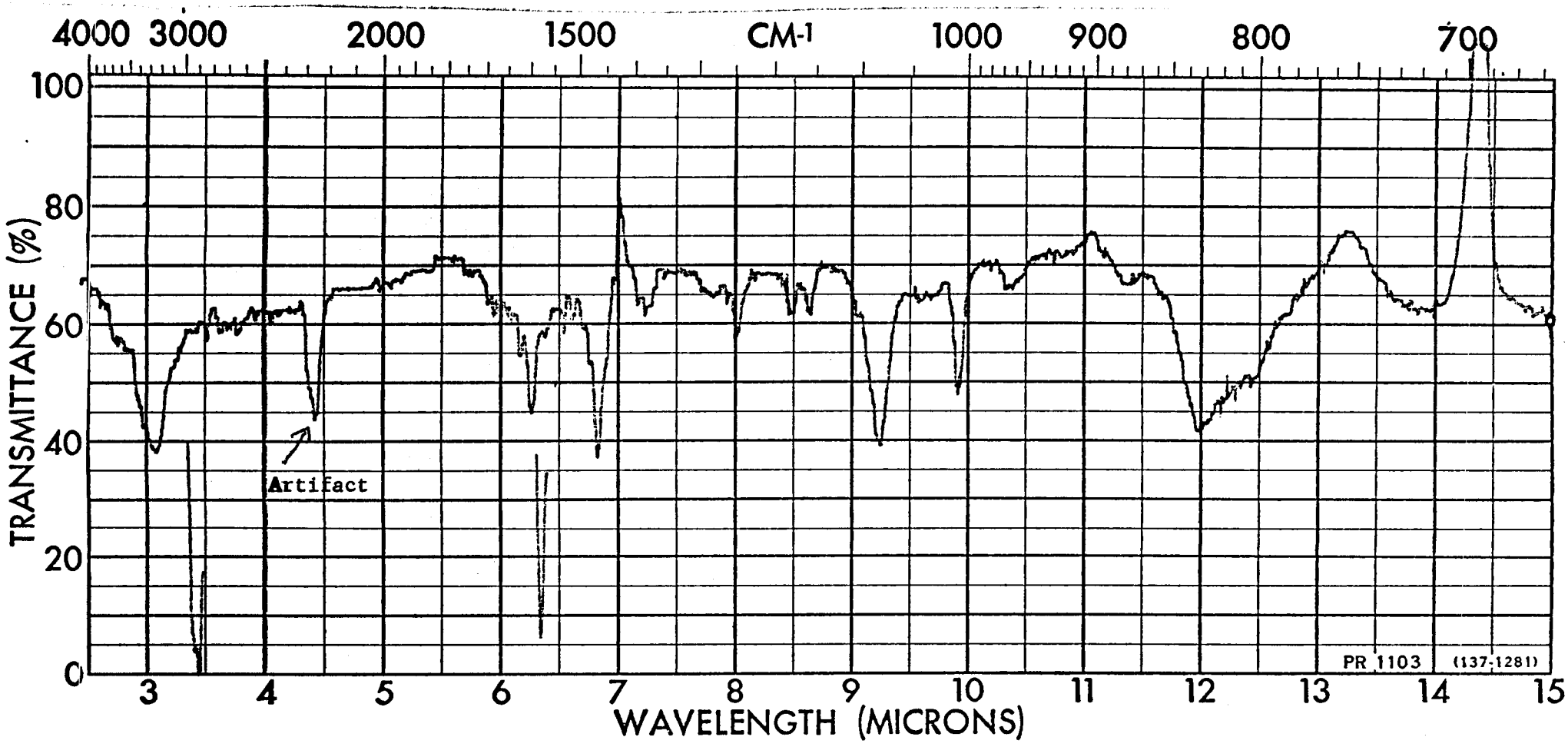
Appendix No. 3



KBr Disc

Solid from Filtrate of EtOH Extraction of DA-39-108

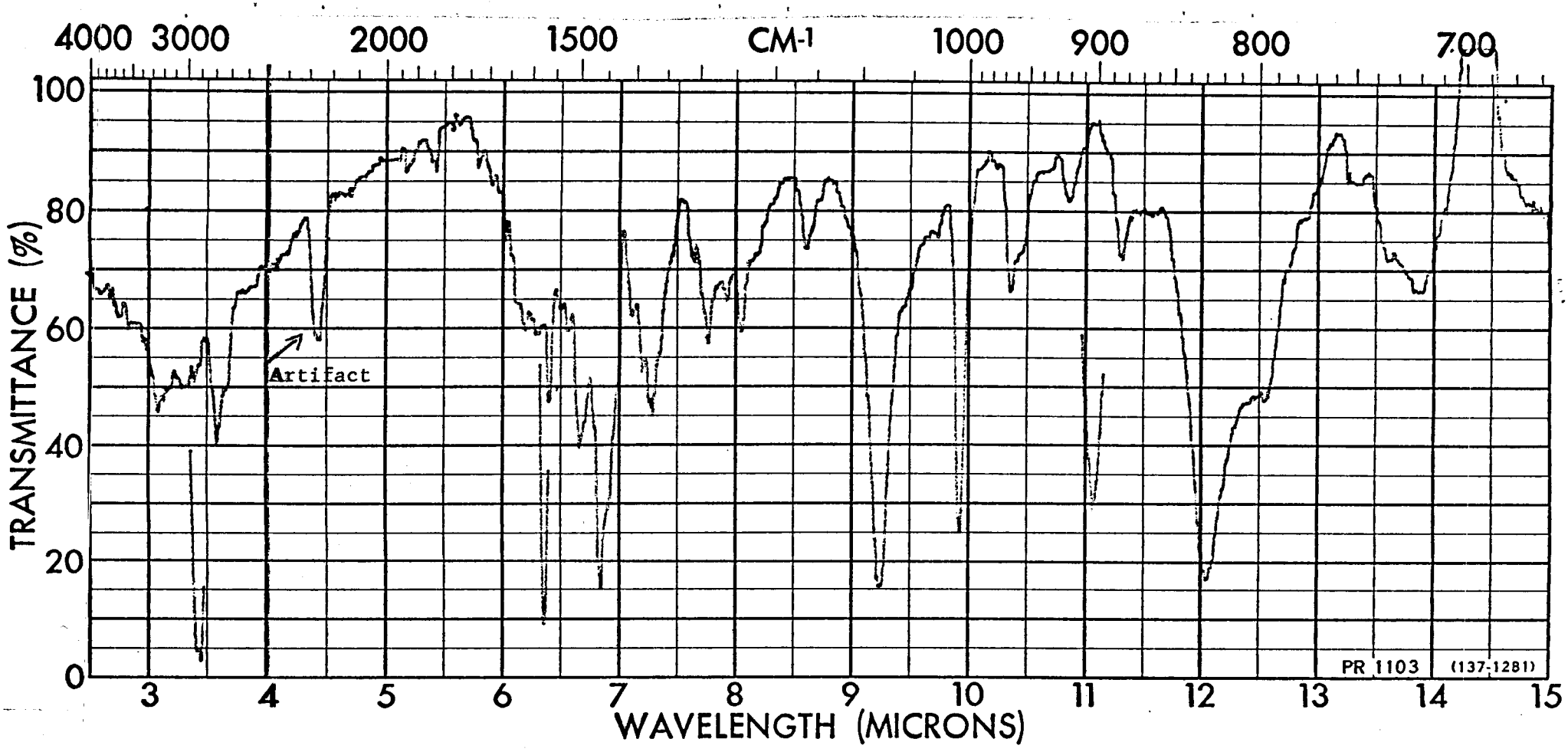
Appendix No. 4



KBr Disc

Solid from Filtrate of EtOH Extraction of DA-39-110

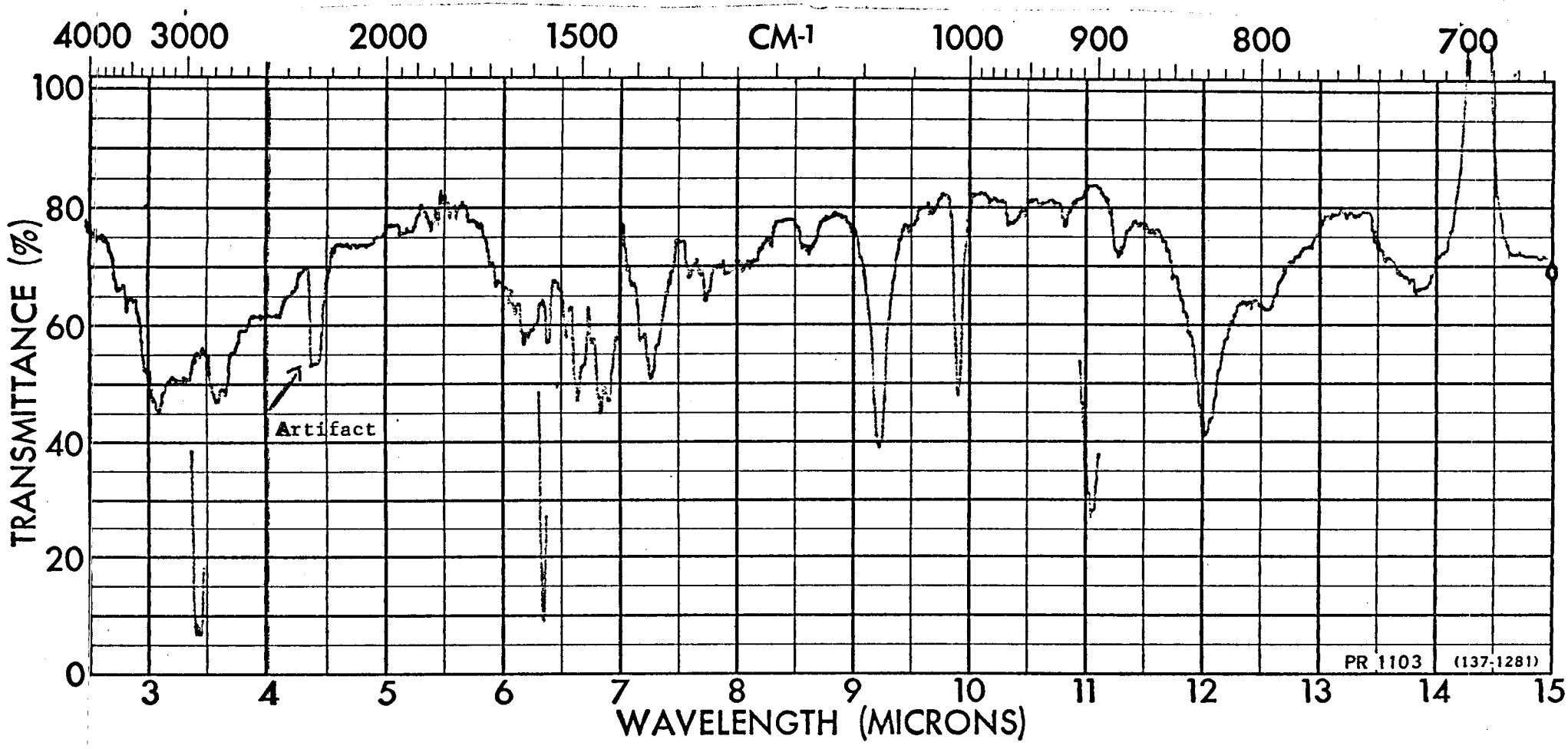
Appendix No. 5



KBr Disc

Solid from Filtrate of EtOH Extraction of DA-39-117

Appendix No. 6



KBr Disc

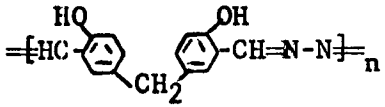
Solid from Filtrate of EtOH Extraction of DA-39-118

Appendix No. 7

PART NO. 950017

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

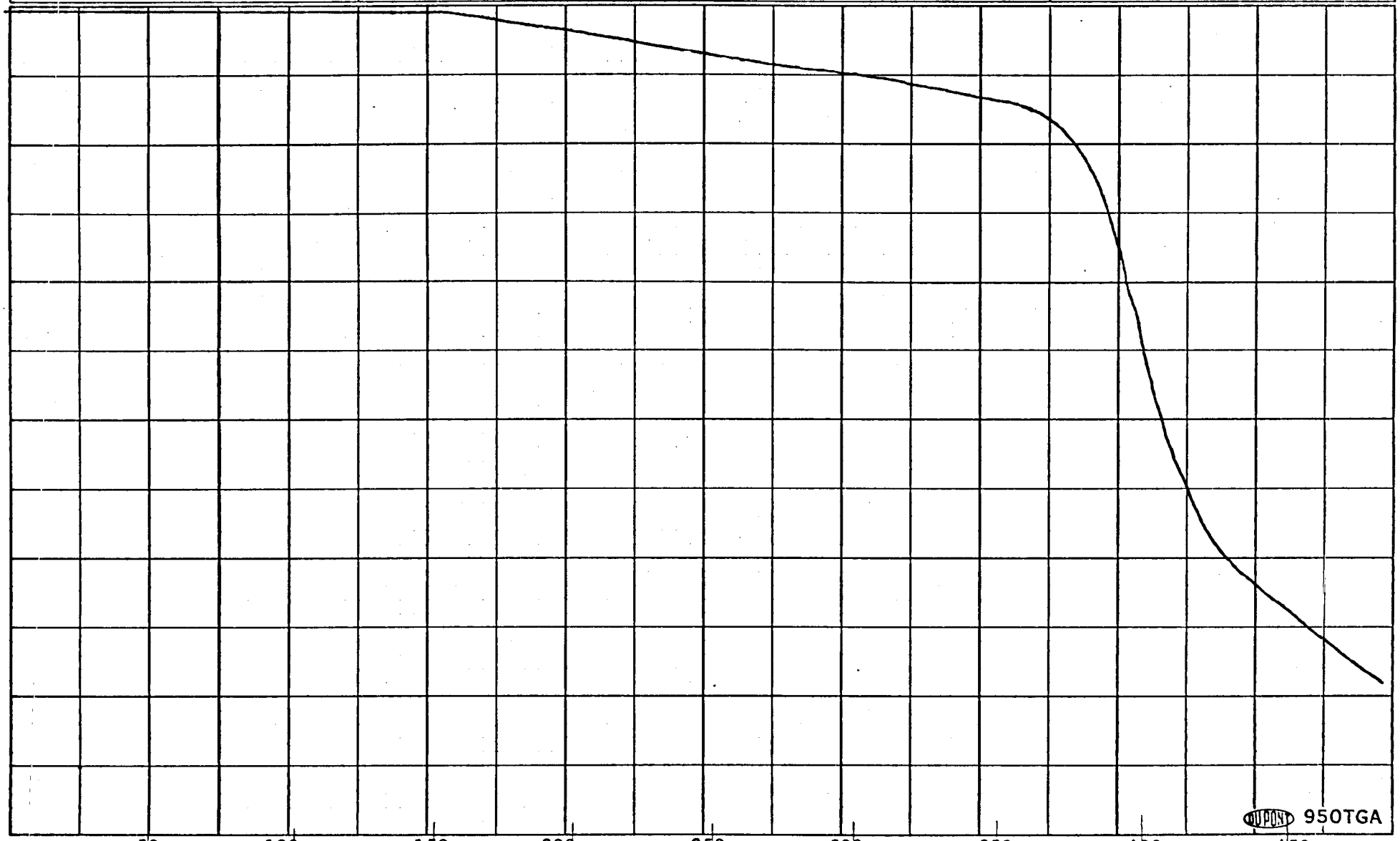
SAMPLE: DA-39-93



Yellow

SIZE 9.87 mg.

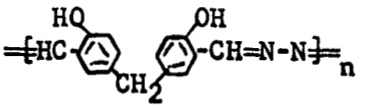
X-AXIS	Y-AXIS	
TEMP. SCALE 50 °C / inch	**SCALE** 0.4 mg. / inch	**RUN NO.** ____ **DATE** ____
SHIFT 0 inch	(SCALE SETTING X 2)	**OPERATOR** RKS
TIME SCALE (ALT.) 0	**SUPPRESSION** 7.47 mg.	**HEATING RATE** 5 °C / min.
		ATM. nitrogen
		TIME CONSTANT 2 sec.



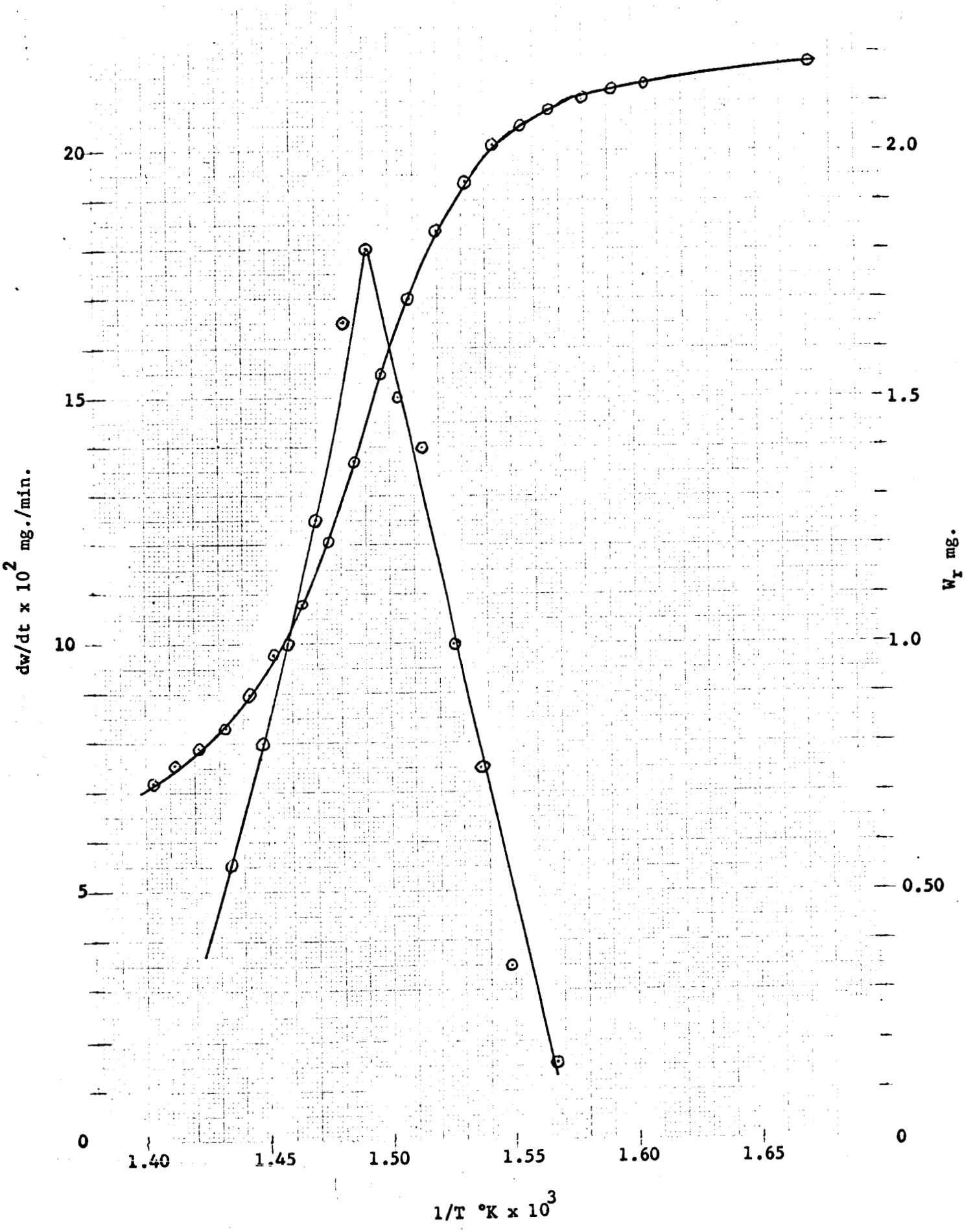
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 8

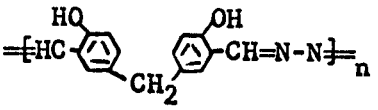
DA-39-93



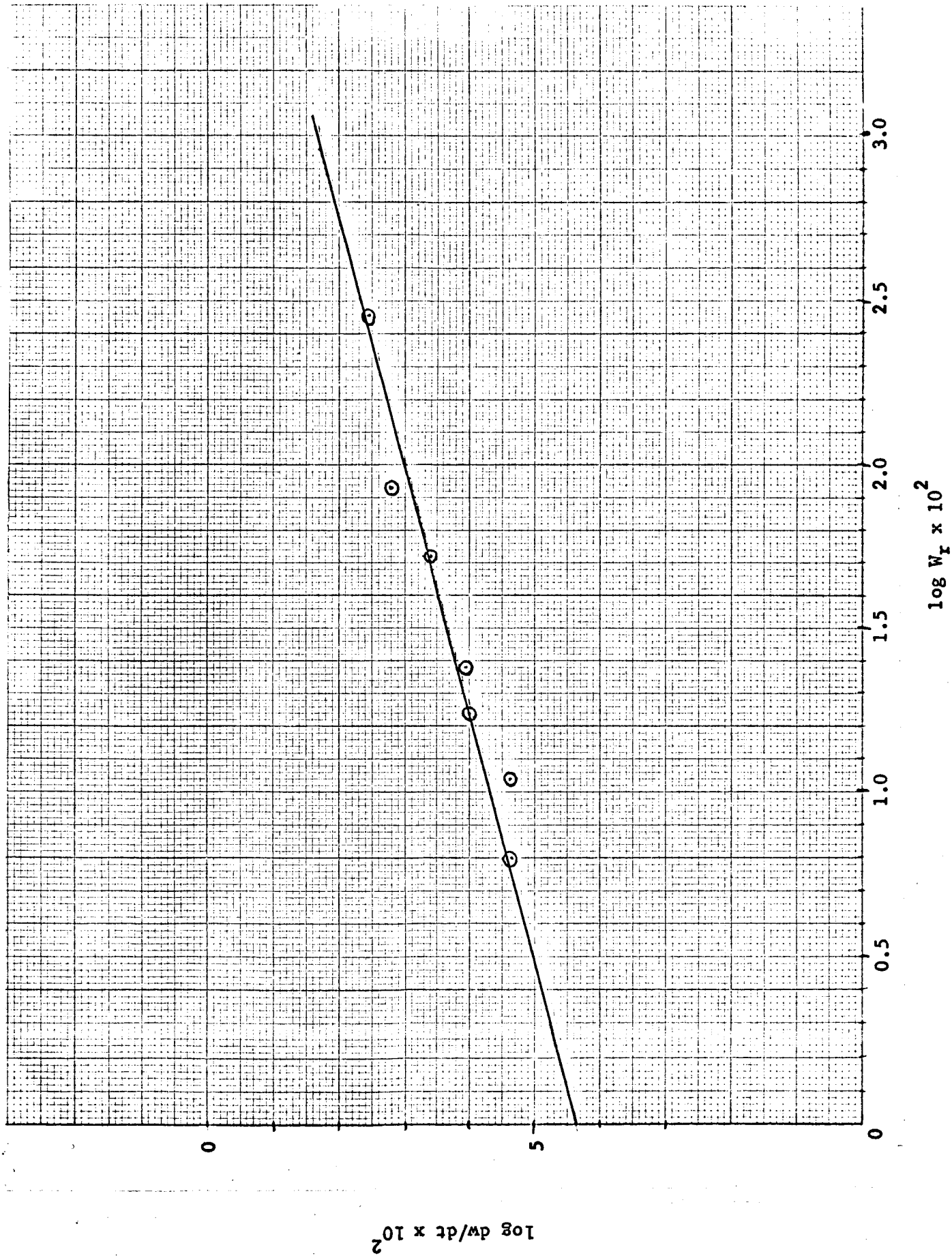
Appendix No. 9



DA-39-93



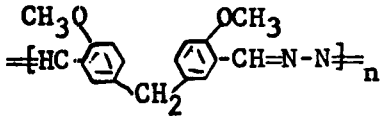
Appendix No. 10



PART NO. 950017

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

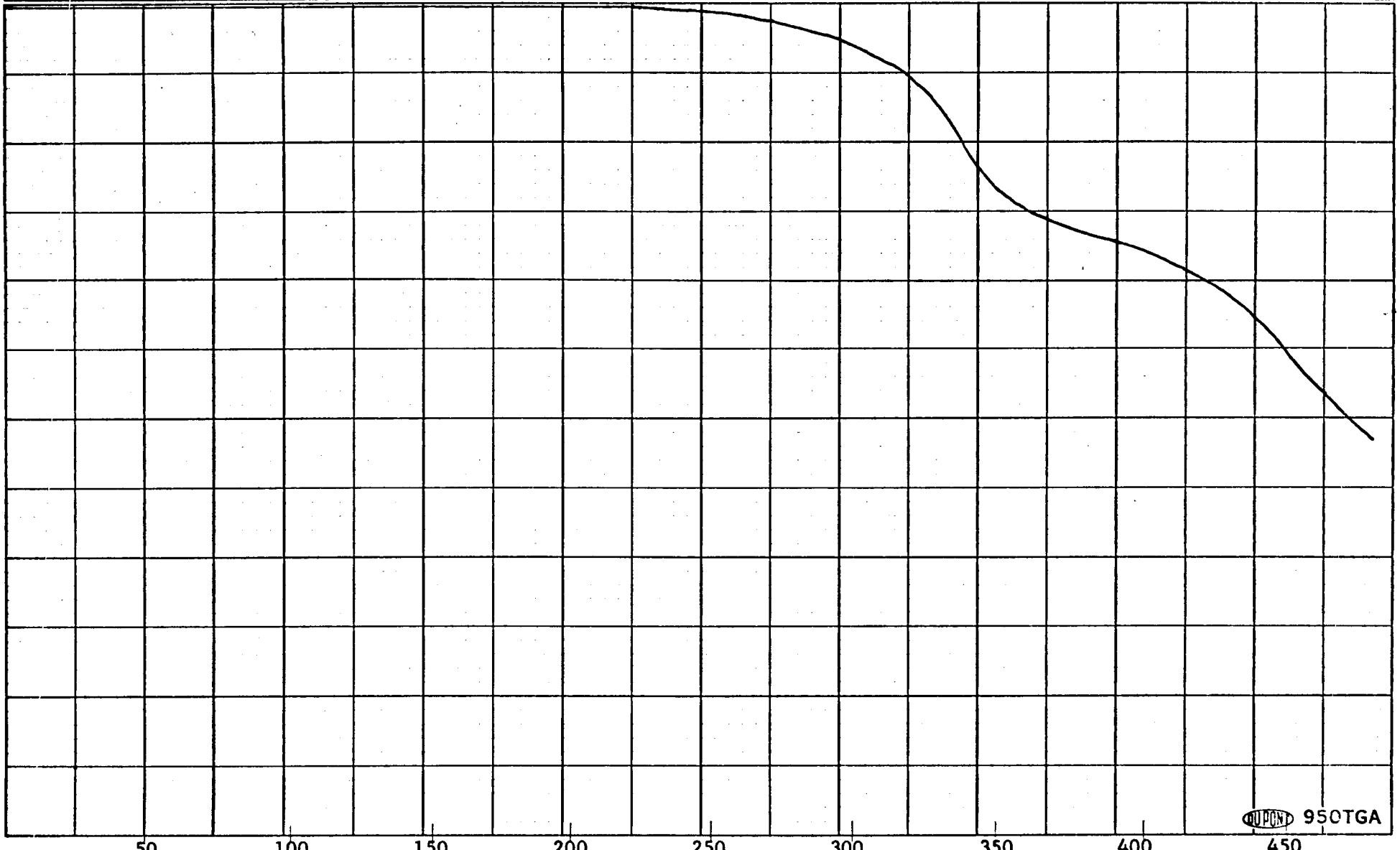
SAMPLE: DA-39-95



Yellow

SIZE 9.93 mg.

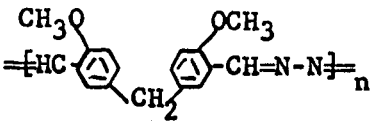
X-AXIS	Y-AXIS	
TEMP. SCALE 50 °C / inch	**SCALE** 1 mg. / inch	**RUN NO.** ____ **DATE** ____
SHIFT 0 inch	(SCALE SETTING X 2)	**OPERATOR** RKS
TIME SCALE (ALT.) 0	**SUPPRESSION** 3.93 mg.	**HEATING RATE** 5 °C / min.
		ATM. nitrogen
		TIME CONSTANT 2 sec.



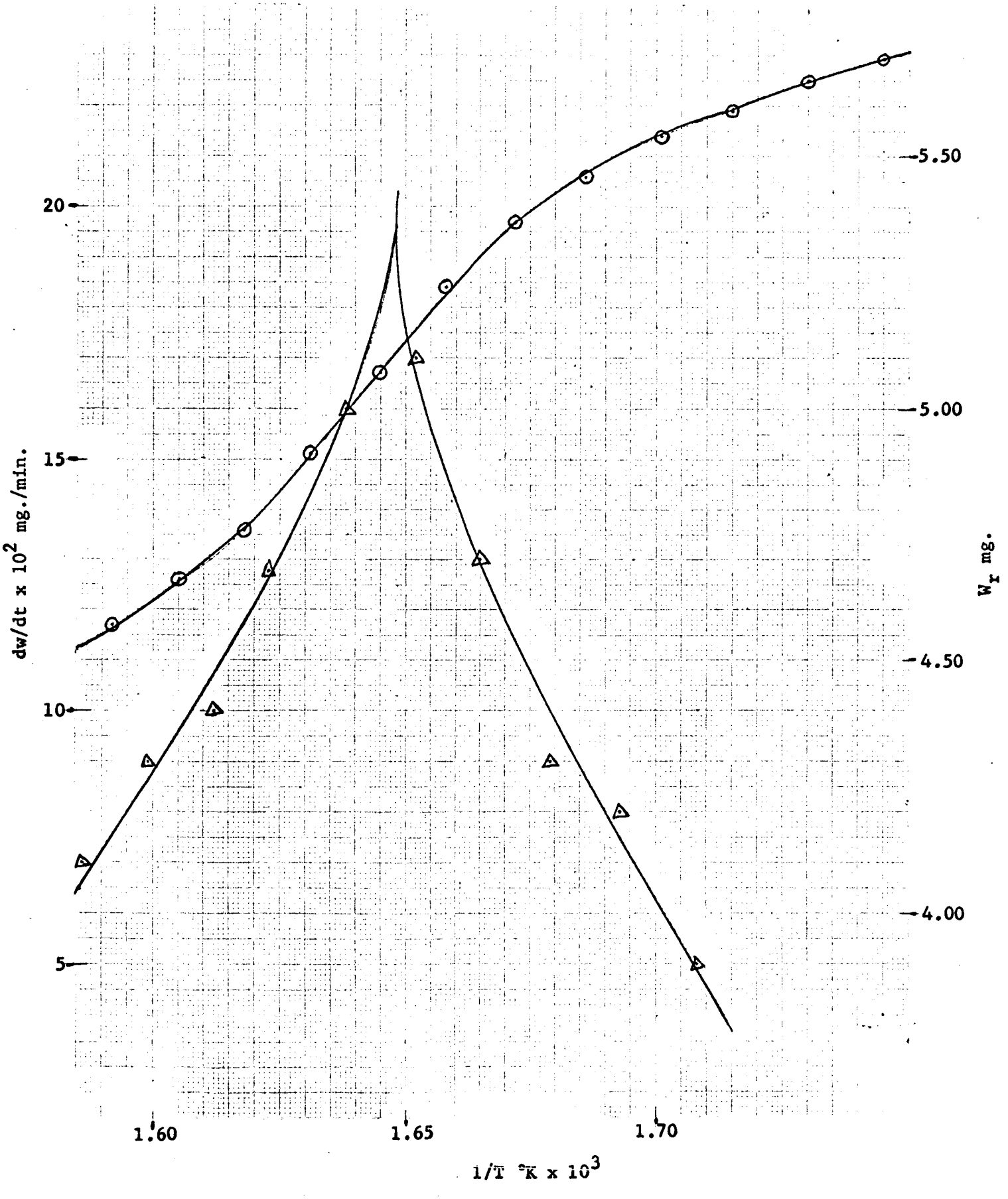
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 11

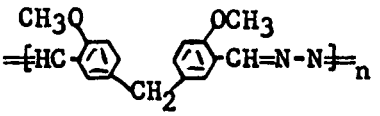
DA-39-95



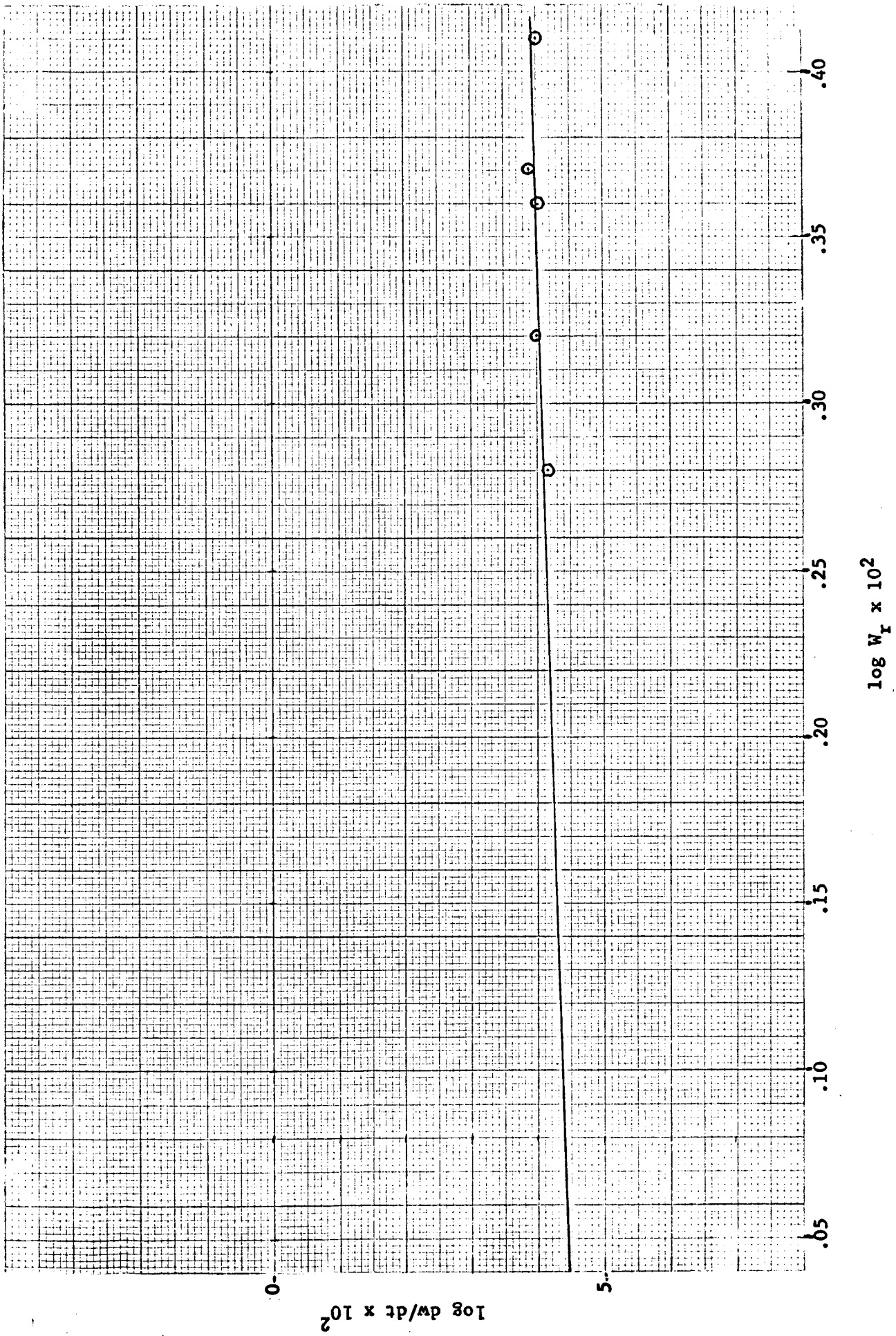
Appendix No. 12



DA-39-95



Appendix No. 13



PART NO 950017

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

SAMPLE: DA-39-43

Black

SIZE 10.08 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 5.08 mg.

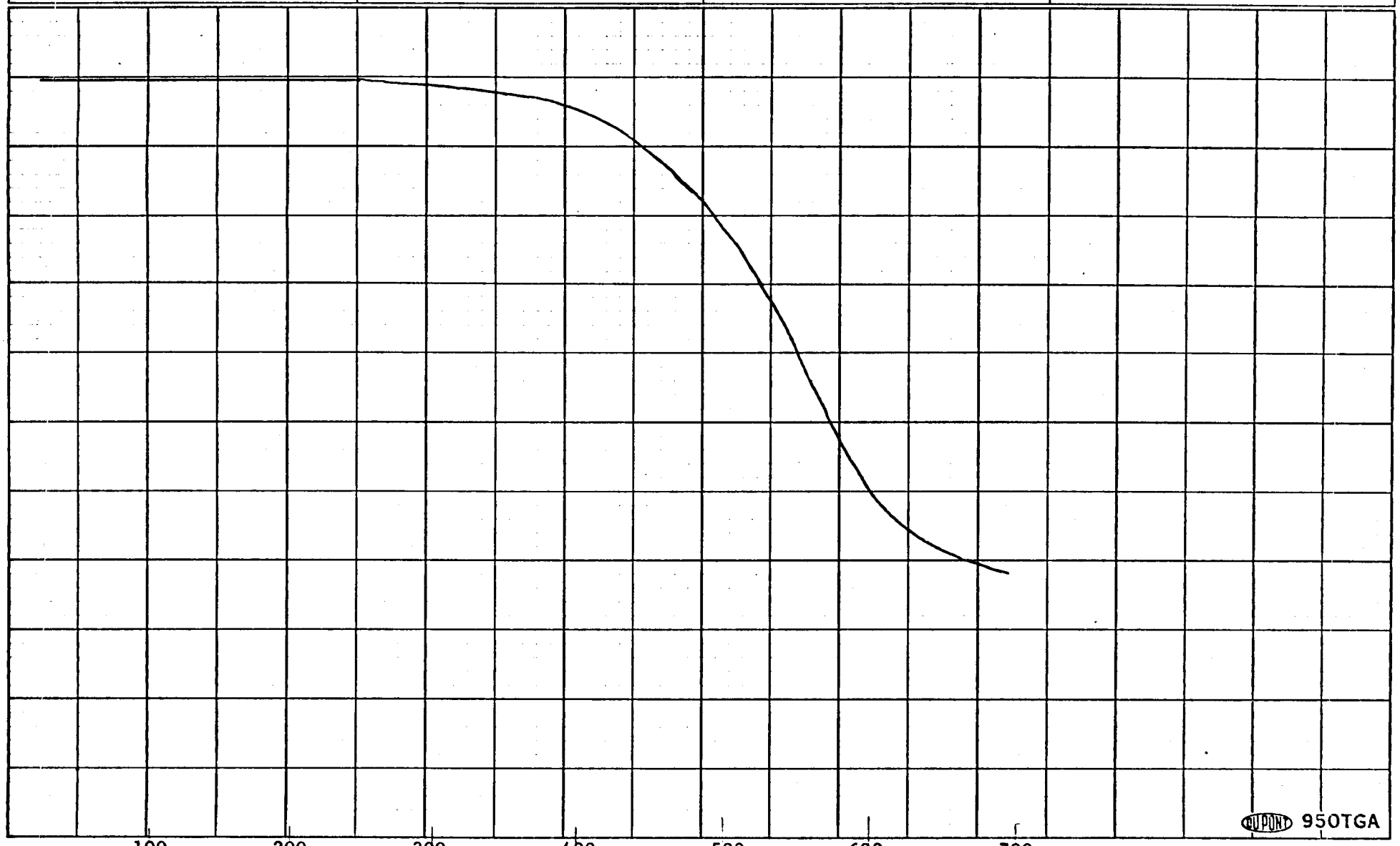
RUN NO. _____ **DATE** _____

OPERATOR RKS

HEATING RATE 5 °C / min.

ATM. nitrogen

TIME CONSTANT 2 sec.



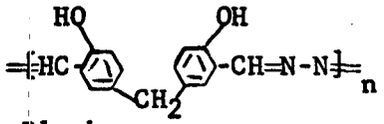
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 14

PART NO. 950017

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

SAMPLE: DA-39-97



Black

SIZE 10.14 mg.

X-AXIS

TEMP. SCALE 100 °C / inch

SHIFT 0 inch

TIME SCALE (ALT.) 2

Y-AXIS

SCALE 1 mg. / inch

(SCALE SETTING X 2)

SUPPRESSION 5.14 mg.

RUN NO. _____ **DATE** _____

OPERATOR RKS

HEATING RATE 5 °C / min.

ATM. nitrogen

TIME CONSTANT 2 sec.

WEIGHT, mg.

100 200 300 400 500 600 700

TEMPERATURE*, °C

DUPONT 950TGA

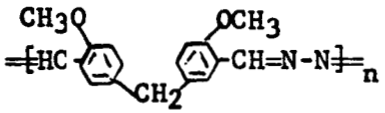
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 15

PART NO. 950017

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

SAMPLE: DA-39-99



Black

SIZE 10.07 mg.

X-AXIS	Y-AXIS	
TEMP. SCALE 100 °C / inch	SCALE 1 mg. / inch	RUN NO. ____ DATE ____
SHIFT 0 inch	(SCALE SETTING X 2)	OPERATOR RKS
TIME SCALE (ALT.) 0	SUPPRESSION 5.07 mg.	HEATING RATE 5 °C / min.
		ATM. nitrogen
		TIME CONSTANT 2 sec.

WEIGHT, mg.

100 200 300 400 500 600 700

TEMPERATURE*, °C

DUPONT 950TGA

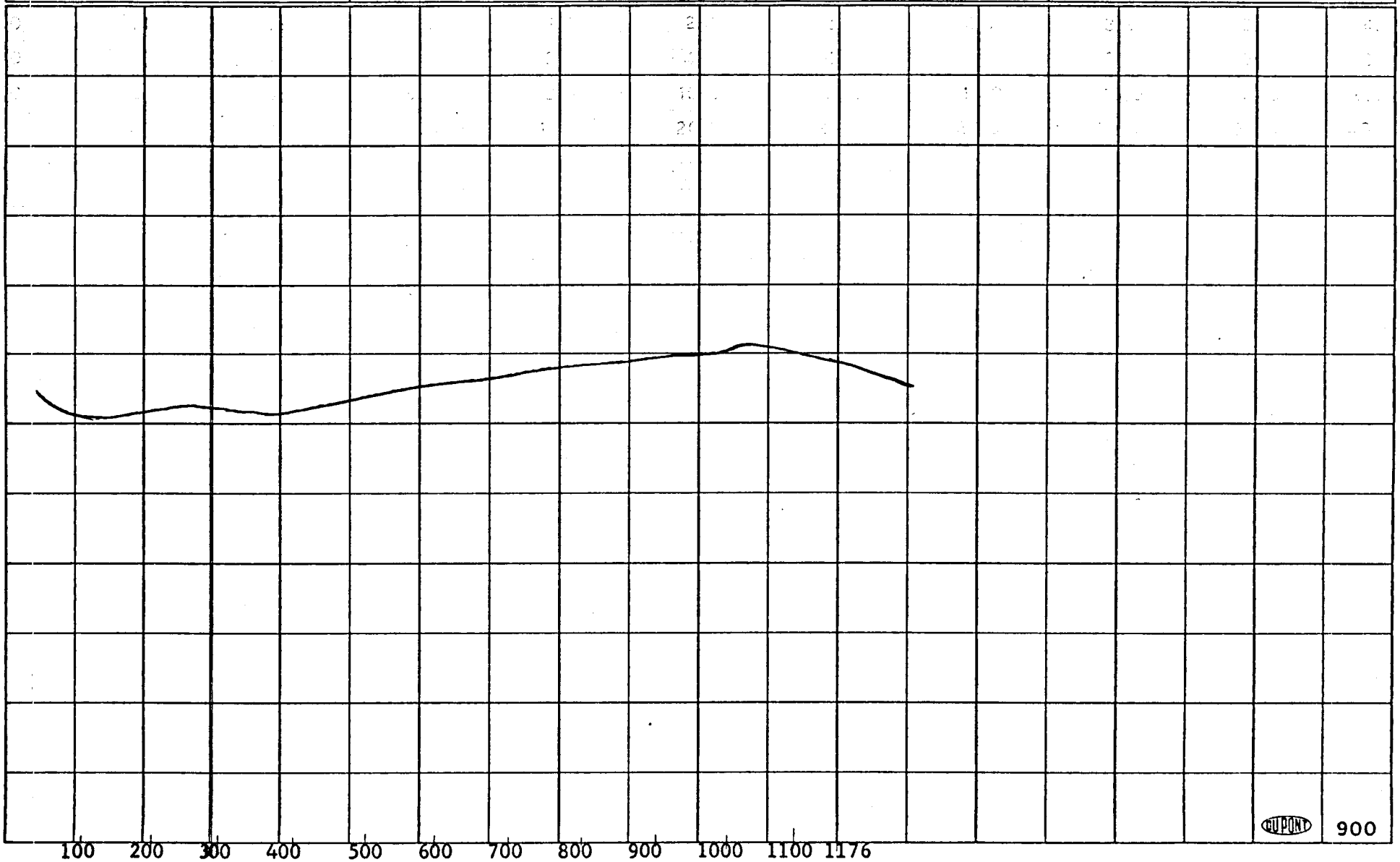
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 16

PART NO. 900303

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

SAMPLE: DA-39-43	SIZE 5 mg.	ATM. nitrogen, 760 MM		RUN NO.
$=\{HC-\langle\rangle-CH=N-N\}_n=$	REF. graphite		T / ΔT	DATE
Black	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



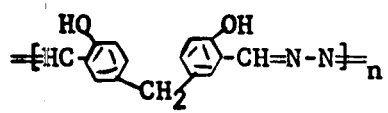
T (MILLIVOLTS: _____ THERMOCOUPLE, REF. JUNCT. _____ °C)

SAMPLE: _____ RUN NO.: _____ Appendix No. 17

PART NO. 900305

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

SAMPLE: DA-39-97



Black

ORIGIN:

SIZE 5 mg.

REF. graphite

PROG. MODE heat

RATE 15 °C/MIN. **START** 25 °C.

ATM. nitrogen, 760 MM

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

RUN NO.

DATE

OPERATOR RKS

BASE LINE SLOPE 0

EXO ↑

ΔT

↓ ENDO

100 200 300 400 500 600 700 800 900 1000 1100 1176

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

DUPONT 900

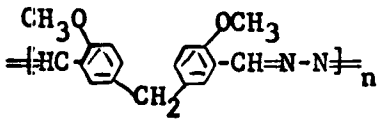
SAMPLE: _____ RUN NO.: _____

Appendix No. 18

PART NO. 900005

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

SAMPLE: DA-39-99



Black

ORIGIN:

SIZE 5 mg

REF. graphite

PROG. MODE heat

RATE 15 °C/MIN., START 25°C.

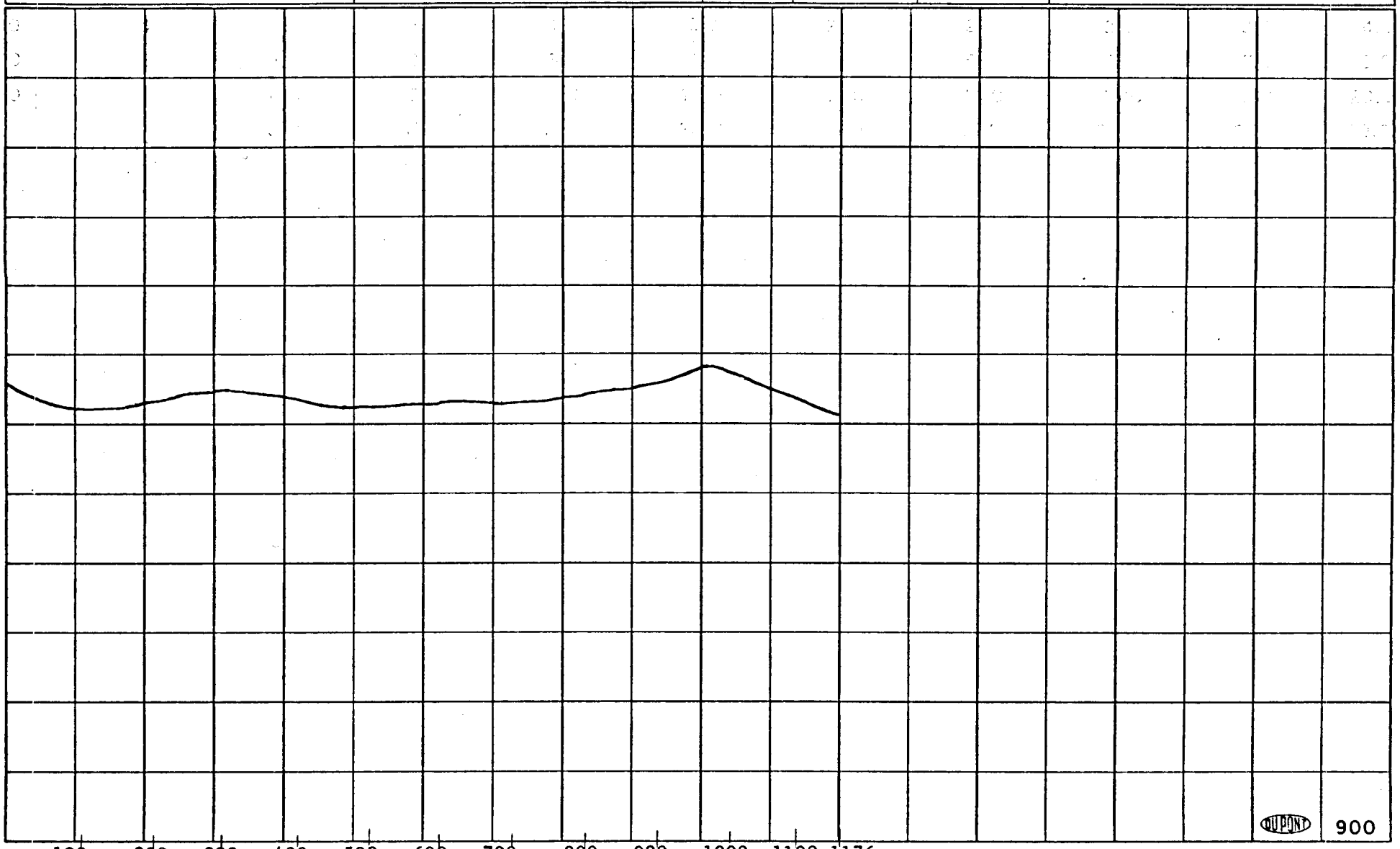
	T	ΔT
ATM. nitrogen, 760 MM		
SCALE	2 MV/IN.	0.04 MV/IN.
SHIFT	0 IN.	0 IN.

RUN NO.

DATE

OPERATOR RKS

BASE LINE SLOPE 0



DUPONT 900

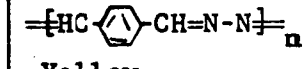
T (MILLIVOLTS: _____ THERMOCOUPLE, REF. JUNCT. _____ °C)

SAMPLE: _____ RUN NO.: _____ Appendix No. 19

PART NO. 950017

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

SAMPLE: DA-32-34



Yellow

1) 10.45; 2) 10.43; 3) 10.50

SIZE _____ 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)

1) 4.45; 2) 4.43; 3) 4.50

SUPPRESSION _____ mg.

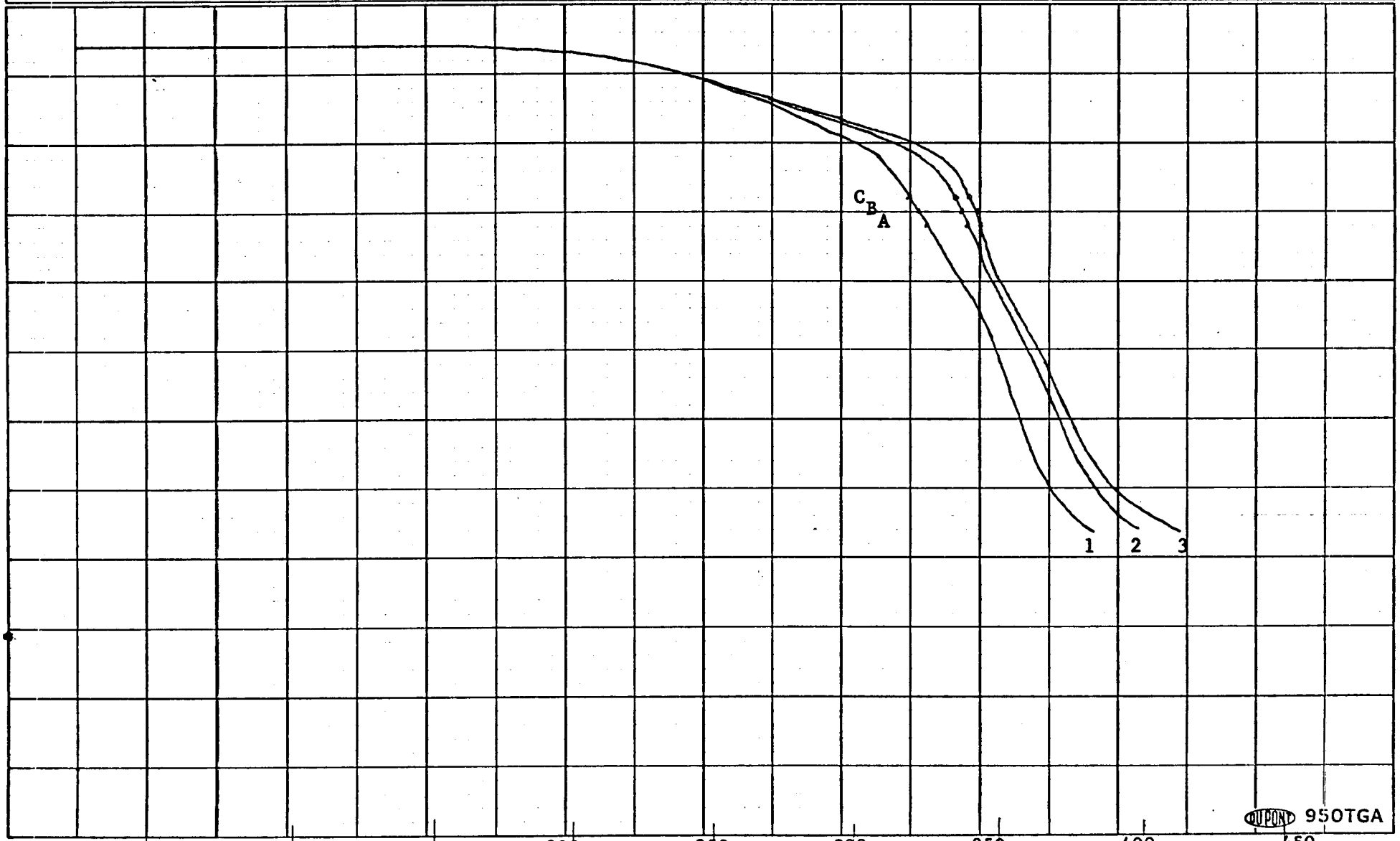
RUN NO. _____ **DATE** _____

OPERATOR RKS

HEATING RATE 1) 5°C 2) 10°C; 3) 15°C °C / min.

ATM. nitrogen

TIME CONSTANT 2 sec.



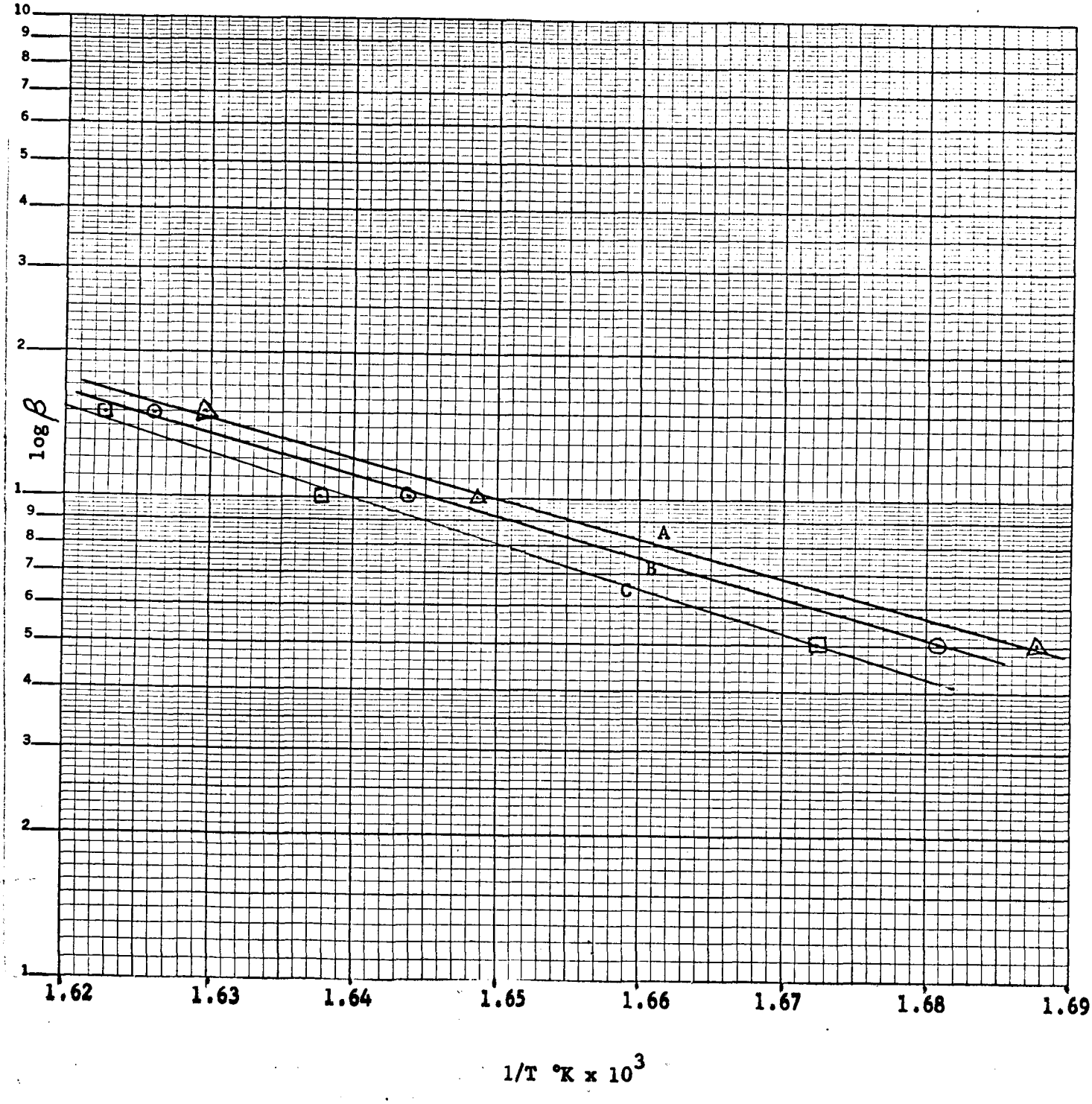
WEIGHT, mg.

50 100 150 200 250 300 350 400 450

TEMPERATURE*, °C

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

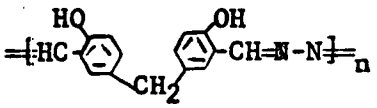
Appendix No. 20


log β
10
9
8
7
6
5
4
3
2
1
A
B
C
1.62
1.63
1.64
1.65
1.66
1.67
1.68
1.69
1/T °K x 10^3

PART NO. 950017

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

SAMPLE: DA-39-93



Yellow

SIZE 1) 1o.28mg. 2) 10.29; 3) 10.31.

X-AXIS

TEMP. SCALE 50 °C / inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

SCALE 1 mg. / inch

(SCALE SETTING X 2)

1) 4.28; 2) 4.29; 3) 4.31.

SUPPRESSION _____ mg.

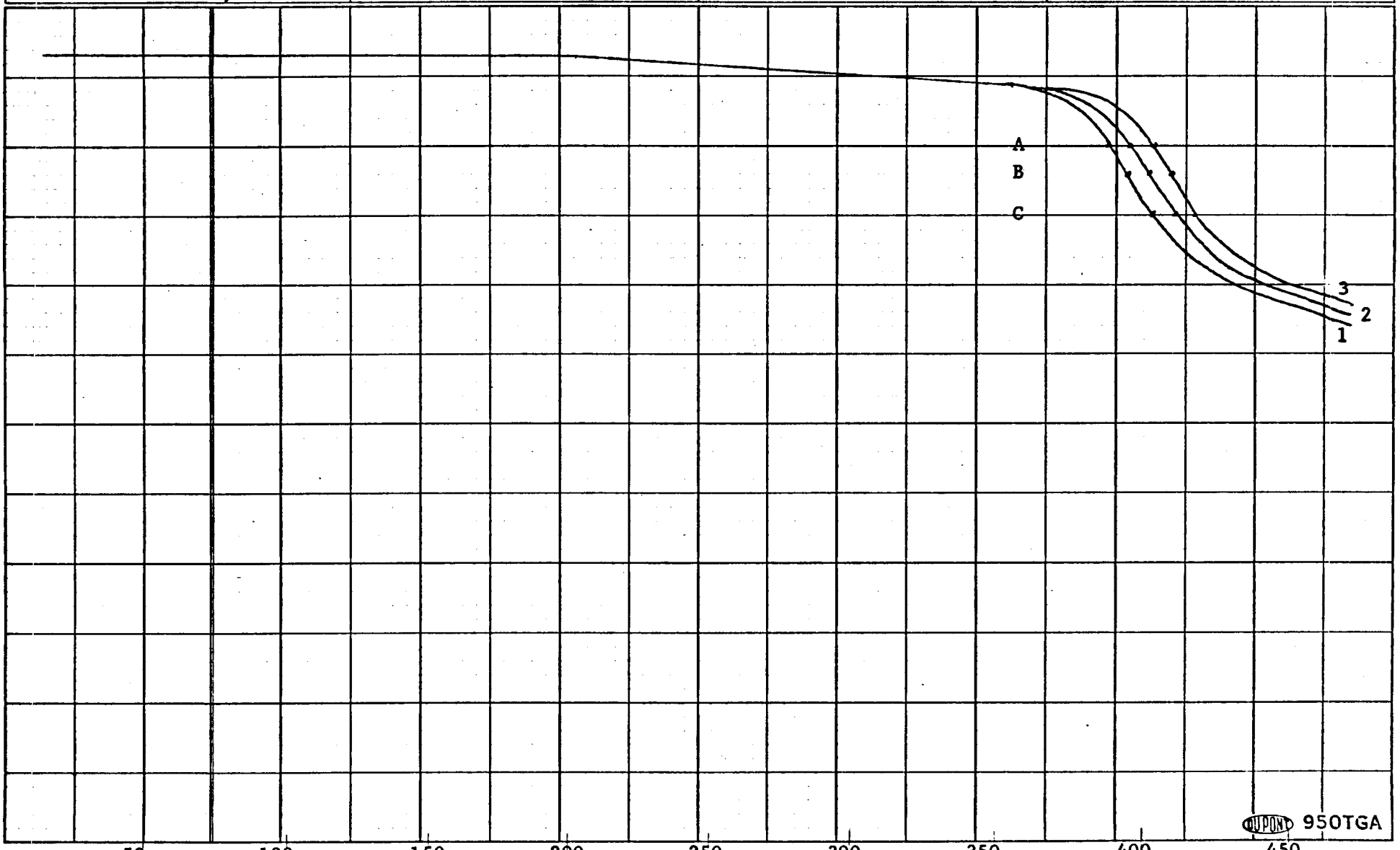
RUN NO. _____ **DATE** _____

OPERATOR RKS

HEATING RATE 1) 10°C 2) 15°C; 3) 30°C. °C / min.

ATM. nitrogen

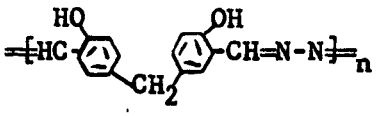
TIME CONSTANT 2 sec.



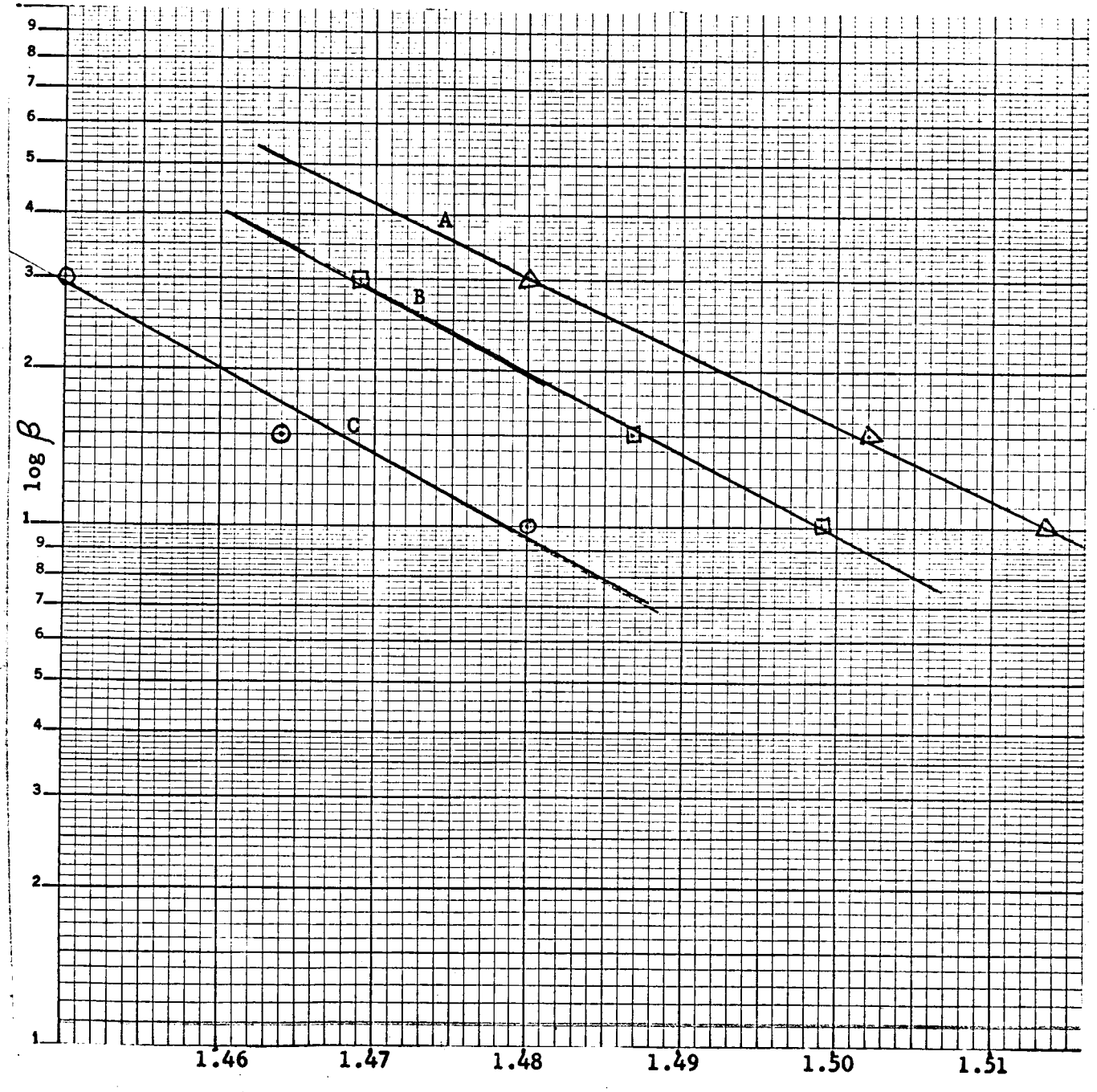
* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Appendix No. 22

DA-39-93



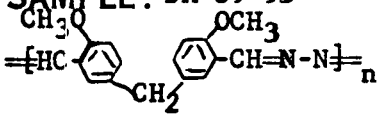
Appendix No. 23



PART NO. 950017

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

SAMPLE: DA-39-95



Yellow

SIZE 1) 11.50; 2) 11.43; 3) 10.68 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) 0

Y-AXIS

SCALE 0.4 mg./inch

(SCALE SETTING X 2)

1) 9.10; 2) 9.03; 3) 8.28

SUPPRESSION _____ mg.

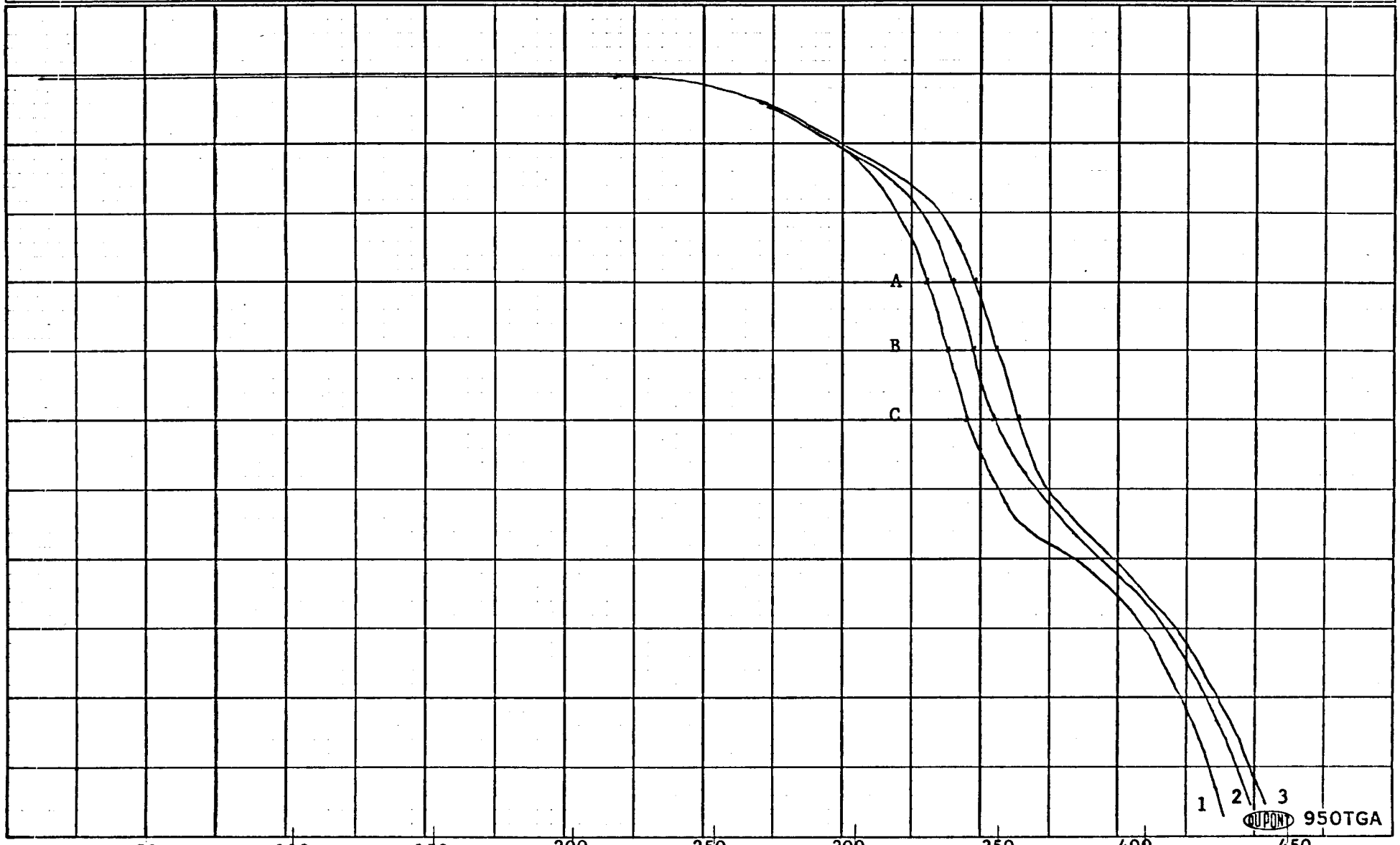
RUN NO. _____ DATE _____

OPERATOR RKS

HEATING RATE 1) 5°C; 2) 10°C; 3) 15°C °C/min.

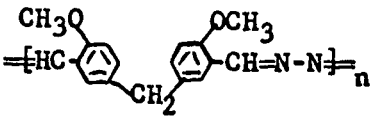
ATM. nitrogen

TIME CONSTANT 2 sec.



Appendix No. 24

DA-39-95



Appendix No. 25